

# FINAL REGISTRATION REPORT

## **Part B**

### **Section 7**

#### **Metabolism and Residues**

Detailed summary of the risk assessment

Product code: CHR/H/CPD 300 SL

Product name(s): Major 300SL, Cloe 300SL, ProSto 300SL

Chemical active substances:

Clopyralid, 300 g/L

Central Zone

Zonal Rapporteur Member State: Poland

Core assessment

(renewal of authorization)

Applicant: Innvigo sp. z o. o.

Submission date: 12.2021; updated 02.2024

MS Finalisation date: 11.2022; 03.2023; 10.2023; 03.2024;  
06.2024

### Version history

When	What
December 2021	New data for CHR/H/CPD based on the renewal of active substance - clopyralid. New data is highlighted in yellow.
November 2022	ZRMs evaluated submitted by Applicant dRR
March 2023	Assessment in relation to comments in the Reporting Table.
October 2023	Verification of the Report in accordance with the Polish National Authority's (Ministry of Agriculture and Rural Development) arrangements regarding the assessment of plant protection products containing the active substance clopyralid..
February 2024	Applicant's update
March 2024	Assessment of updated Part B7
June 2024	III commenting round

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## 7 Metabolism and residue data (KCA section 6)

### 7.1 Summary and zRMS Conclusion

October 2023 Verification of the Report in accordance with the Polish National Authority's (Ministry of Agriculture and Rural Development) arrangements, from the meeting regarding the assessment of plant protection products containing the active substance clopyralid (4.10.2023).

March 2024 Assessment of the new data (marked in green).

The applicant provided the new residue trials. The dark blue background of the new data provided by the applicant has been changed by zRMS to a lighter one to increase the readability of the text.

#### Stability of residues during storage of samples

Stability of residues during storage of samples was provided during the EU review of clopyralid.

Residues of clopyralid were found to be stable at  $\leq -18^{\circ}\text{C}$  for up to:

13 months in maize fodder and forage (high water content matrix)

13 months in maize grain (high starch content matrix)

17 months in pasture grass (high water content matrix)

24 months in rape seed (high oil content matrix)

#### Metabolism in plants and animals

Residue definition for monitoring (Commission Regulation (EU) 2021/1807 of 13 October 2021): clopyralid (plants and animals)

Proposed residue definition for monitoring (EFSA Journal 2021;19(1):6389): clopyralid common moiety (sum of clopyralid, its salts and conjugates expressed as clopyralid) (applicable only for cereals/grass).

The proposed change will not have an impact on the existing MRLs, as the analytical methods used to generate data for risk assessment and for enforcement include a hydrolysis step which is capable to cover the common moiety.

Residue definition for risk assessment:

Clopyralid common moiety (sum of clopyralid, its salts and conjugates expressed as clopyralid) – pending the outstanding clarification on the nature of “polar clopyralid” (EFSA Journal 2018;16(7):5389)

During the peer review, the data gap related to the identification of an unknown compound observed in sugar beet and oilseed rape metabolism studies was identified.

EFSA Journal 2021;19(1):6389:

*Based on the metabolic pattern identified in metabolism studies with cereals, rotational crops and the results of hydrolysis studies, the residue definitions were proposed as clopyralid common moiety (sum of clopyralid, its salts and conjugates expressed as clopyralid) both, for enforcement and risk assessment. These residue definitions are applicable to cereals/grass crop group, rotational crops and processed products.*

*Since the clarification of the unknown polar metabolite (called ‘polar clopyralid’) in mature sugar beet and oilseeds identified by the EU pesticides peer review was not sufficiently addressed under the current assessment, EFSA concludes that the proposed residue definitions are applicable only to cereals/grass crop group for which a new metabolism study was submitted under the current assessment and for which the data gap identified by the peer review is not relevant. For remaining crop groups, the data gap as identified by the EU pesticides peer review remains open.*

#### Authority's arrangements:

*- in the case of clopyralid, assessment of residue data for the uses proposed by the Applicants, including, among others, on oilseeds, roots or tubers (crops other than representative crops assessed in RAR (2019) for the substance clopyralid) should be carried out in accordance with the general residue definition for clopyralid proposed by EFSA in the document EFSA Journal 2018;16(8):5389 - applies all administrative proceedings conducted by the Ministry of Agriculture and Rural Development (Article 33, Article 43, Article 40, Article 45, Article 51).*

#### Plant residue definition for monitoring: Clopyralid (Reg. (EU) 2021/1807)

Plant residue definition for risk assessment: clopyralid common moiety (sum of clopyralid, its salts and conjugates expressed as clopyralid) – pending the outstanding clarification on the nature of “polar clopyralid” (EFSA Journal 2018;16(7):5389).

~~According to EFSA, the residue definition should be limited to cereals/grass only. Taking this into account, application on winter rape and sugar beet are not acceptable until the data gap is filled.~~

The intended uses **on cereals** are supported by the evaluated plant metabolism studies.

One new hydrolysis study was evaluated as equivalent to protected hydrolysis study and was accepted in data matching (Finland 2022): K. Hamnett; 2019; Study no: FR/001648 which is equivalent to Adusumilli, H. 2014; study no: 140574. The test compound clopyralid was stable under all conditions of high temperature hydrolysis for simulation of food processing. Equivalent endpoint has been received.

New metabolism study in rotational crops was evaluated as equivalent to protected study and was accepted in data matching (Finland 2022): Hall, L. R.; 2015; DAS Study No. 130733 to which is equivalent Rooney P., 2021, [14C]-Clopyralid Metabolism in Rotational Crops FR/001647. The requirement for alternative tests has been met.

NOTE: the new alternative studies have not been assessed in this application.

#### Magnitude of residues in plants

##### Winter wheat

Proposed uses: 1 application, BBCH 20-29 (Spring), 120 g as/ha, PHI: not required

Applicant refers to the unprotected EU data. GAP on which EU a.s. assessment is based: 1 x 0.150 kg as/ha, BBCH 39.

No new data are submitted in the framework of this application. Presented data are still valid and meet criteria of current guidelines.

Sufficient trials are available to support the proposed use. The residues arising from the proposed uses will not exceed the MRLs established for wheat (Reg. (EU) 2021/1807).

##### Winter rape, Sugar beet, *Beta vulgaris* (beetroots)

~~According to EFSA (EFSA Journal 2021;19(1):6389), the residue definition should be limited to cereals/grass only. Taking this into account, application on winter rape and sugar beet are not acceptable (until the data gap is filled).~~

##### Winter rape

Proposed use: 1 application, BBCH: till 50, 120 g as/ha, PHI: not required

1 application, BBCH: till 50 or 20-21, 90 g as/ha, PHI: not required (mixed with CHR/H/PCR and

## CHR/H/MTC).

Applicant refers to unprotected EU data:

Trials GAP: 1 x 0.1 kg as/ha + 1 x 0.2 kg as/ha, BBCH:51; outdoor

Residues: <0.01, 0.01, 2 x 0.02, 0.03, 0.04, 0.05, 0.1 mg/kg

Sufficient data are available to support the proposed use. The residues arising from the proposed uses will not exceed the MRLs established for oilseed rape (Reg. (EU) 2021/1807).

Sugar beet, *Beta vulgaris*

Proposed use: 1 application, BBCH 12-14 (Spring), 120 g as/ha, PHI: not required

3 applications, BBCH 12-14 (Spring), 60 g as/ha, PHI: not required

Applicant refers to unprotected EU data:

Trials GAP (sugar beets): 1 x 0.1 kg as/ha + 1x 0.2 kg/ha latest timing of BBCH 39

Residues: 0.12, 0.17, 0.21, 0.29, 0.34, 0.35, 0.36, 0.41, 0.56, 0.80 mg/kg

According to the SANTE/2019/12752 rev.1 extrapolation from sugar beets (0900010) is possible to beet-roots (0213010).

Sufficient data are available to support the proposed uses. The residues arising from the proposed uses will not exceed the MRLs established for sugar beet roots (Reg. (EU) 2021/1807).

March 2024

The applicant provided the new residue trials.

Sugar beet

The objective of the studies were to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Sugar beet raw agricultural commodity (RAC) after one foliar application (at BBCH 14) of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.5 L/ha. Nine independent trials (North France, Germany, Hungary, Czech Republic and Poland) are accepted and valid in relation to storage stability data. Residues are below MRL established for sugar beet roots (Reg. (EU) 2021/1807).

Oil seed rape

The objective of the studies were to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in oil seed rape raw agricultural commodity (RAC) after one foliar application (at BBCH 51) of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha. Eight independent trials (Czech Republic, Germany, Poland and Netherland) are accepted and valid in relation to storage stability data. Residues are below MRL established for oil seed rape (Reg. (EU) 2021/1807).

Wheat

The objective of the studies were to determine the residue levels of Clopyralid (Sum of Clopyralid, its salts and conjugates) in winter wheat raw agricultural commodity (RAC) after one foliar application (at BBCH 29) of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha. Eight independent trials (Czech Republic, Germany, Poland and France) are accepted and valid in relation to storage stability data. Residues are below MRL established for wheat (Reg. (EU) 2021/1807).

## Livestock feeding studies

New Dietary Burden calculations were performed, taking into account STMR and HR values from residues trials on CHR/H/CPD 300 SL (using Animal model 2017).

According to EFSA Journal 2018;16(7):5389 livestock feeding studies are performed during Annex I inclusion and renewal. No new livestock studies feeding studies are necessary. There is no risk for animal

MRLs to be exceeded.

March 2024

New Dietary Burden calculations were performed, taking into account STMR and HR values for Sugar beet, Wheat and Oilseed rape from new residues trials on Faworyt 300 SL / CHR.H/CPD 300 SL. The new calculation results do not change the conclusions.

#### Magnitude of residues in processed commodities

New, alternative to the protected study was provided by the applicant (White T., 2021, S19-01810; White T., 2021, S20-04397) and was accepted in data matching (Finland 2022). No further data is required.

NOTE: new alternative study has not been assessed in this application.

#### Rotational study

According to the available data following label restriction is proposed: not to use clopyralid on the same field for 125 days after the initial application regardless of the crop grown (see EFSA Journal 2021;19(1):6389).

#### Other / special studies

Clopyralid is systemic compound and potential residues in honey might occur in honey even from applications before flowering. Therefore, information about residue level in pollen and bee products should be provided by the applicant (post registration requirement).

05.2024 III commenting round

As follows from comment contained in *Reporting table Part A and B for Major 300 SL after III commenting round*, one of member state does not agree to authorization of the intended use (oilseed rape – melliferous crop) until the new MRL has been set for honey. zRMS considers that the decision on the possibility of authorizing the use on rapeseed can be made at the level of a Member State.

Taking into account the date of submission of the documents and the date of application of the product shown in the GAP Table, the missing data may be required after registration of the plant protection product. In accordance with the arrangements in place in Poland, Poland agrees to such intended use provided that the study is performed after registration (post-registration requirement).

#### Estimation of exposure through diet and other means

The **accepted proposed** uses of clopyralid in the formulation CHR.H/CPD 300 SL do not represent unacceptable acute and chronic risks for the consumer. Applicant's calculations are accepted (EFSA PRIMo rev 3.1).

March 2024

New consumer calculations were performed considering STMR/HR values from newly submitted residue studies on Sugar beet., Oilseed rape and Wheat. The new calculation results do not change the conclusions.

### 7.1.1 Critical GAP(s) and overall conclusion

#### Selection of critical uses and justification

The critical GAPs with respect to consumer intake and risk assessment for the preparation CHR.H/CPD 300 SL are presented in Table 7.1-1. They have been selected from the individual GAPs in the zone for sugar beets, winter oilseed rape, winter wheat. A list of all intended uses within the zone is given in Part B, Section 0.

The critical GAP was selected from the worst case use on sugar beet, winter oilseed rape and winter wheat of plant protection product CHR/H/CPD 300 SL and highest maximum rate of 0.120 kg of clopyralid.

### Overall conclusion

The data available is considered sufficient for risk assessment. EFSA (2021) concluded that the residue definitions only apply for the crop groups cereals and grass.

#### Authority's arrangements:

*- in the case of clopyralid, assessment of residue data for the uses proposed by the Applicants, including, among others, on oilseeds, roots or tubers (crops other than representative crops assessed in RAR (2019) for the substance clopyralid) should be carried out in accordance with the general residue definition for clopyralid proposed by EFSA in the document EFSA Journal 2018;16(8):5389 - applies all administrative proceedings conducted by the Ministry of Agriculture and Rural Development (Article 33, Article 43, Article 40, Article 45, Article 51).*

As far as consumer health protection is concerned, zRMS agrees with the authorization of the use on winter wheat.

An exceedance of the current MRL for clopyralid in wheat, oilseed rape, sugar beets and beetroots as laid down in Reg. (EU) 2021/1807 is not expected.

The chronic and the short-term intakes of clopyralid residues are unlikely to present a public health concern.

As far as consumer health protection is concerned, agrees with the authorization of the intended use(s).

~~According to available data, no specific mitigation measures should apply.~~

According to the available data following label restriction is proposed: not to use clopyralid on the same field for 125 days after the application regardless of the crop grown.

Crop	MRL[mg/kg]
Oilseed rape	0.5
Sugar beets beetroots	1
Winter wheat	3

### Data gaps

#### Noticed data gaps are:

- Information about residue level in pollen and bee products should be provided by the applicant (post registration requirement)\*
- Data gap on residue definitions should be filled at EU level.
- In the Data Matching Table, Final conclusion, Finland 2022, in case following DAS studies: Study No. 120602, Study No. 130202, Study No. 130906, DAS Study No. 150031 and DAS Study No. 150030 it is stated that above mentioned studies are vertebrate studies, therefore a letter of access has been requested. As the applicant refers to these studies, the letter of access should be provided before the registration of the plant protected product.

\* Taking into account the date of submission of this document and the time of application, the missing data may be required after registration of the plant protection product (according to the Authority's

arrangements).

Regarding missing data on residues in honey the decision on the possibility of authorizing the use on rapeseed can be made at the level of a Member State.

March 2024

The provided studies on beet, rapeseed and wheat do not change the conclusions of the evaluation.

**Table 7.1-1: Acceptability of critical GAPs (and respective fall-back GAPs, if applicable)**

1	2	3	4	5	6	7	8	9	10	11	12	13	14
Use- No. (e)	Member state(s)	Crop and/ or situa- tion  (crop destination /purpose of crop)	F, Fn, Fpn G, Gn, Gpn or I	Pests or Group of pests con- trolled  (additionally: developmental stages of the pest or pest group)	Application				Application rate			PHI (days)	Remarks:  e.g. g safen- er/synergist per ha (+)
					Method / Kind	Timing/ Growth stage of crop & season	Max. number a) per use b) per crop/ season	Min. inter- val between applications (days)	kg or L product/hL a) max. rate per appl. b) max. total rate per crop/season	g or kg as/ha a) max. rate per appl. b) max. total rate per crop/season	Water L/ha  min/ max		
Zonal uses (field or outdoor uses, certain types of protected crops)													
1	PL, CZ, RO, SLO, SK, LT, LV	Winter oilseed-rape Brassica napus; (BRSNW)	F	broadleaf weeds	Spray; medium sprayer	till BBCH 50	a) — 1 b) — 1	n/a	a) — 0.4 b) — 0.4	a) — 0.12 b) — 0.12	200- 300	n/a	N
2	HU	Winter oilseed-rape Brassica napus; (BRSNW)	F	broadleaf weeds	Spray; medium sprayer	till BBCH 51	a) — 1 b) — 1	n/a	a) — 0.4 b) — 0.4	a) — 0.12 b) — 0.12	200- 300	n/a	N
3	PL, CZ, RO	Winter oilseed-rape Brassica napus; (BRSNW)	F	annual and perennial broadleaf weeds	Spray; medium sprayer	till BBCH 50	a) 1 b) 1	n/a	a) — 0.078+0.3 b) — 0.078+0.3 CHR/H/PCR* + CHR/H/CPD*	a) — 0.0234+0.09 b) — 0.0234+0.09 CHR/H/PCR* + CHR/H/CPD*	200- 300	n/a	n
4	PL, CZ, RO	Winter oilseed-rape Brassica napus; (BRSNW)	F	annual and perennial broadleaf weeds	Spray medium sprayer	Autumn BBCH 20-21	a) — 1 b) — 1	n/a	a) — 0,078+0,3+1.5 b) — 0,078+0,3+1.5 CHR/H/PCR* + CHR/H/CPD* + CHR/H/MTC*	a) — 0.0234+0.09+0.750 b) — 0.0234+0.09+0.750 CHR/H/PCR* + CHR/H/CPD* + CHR/H/MTC*	200- 300	n/a	N
5	PL, CZ, RO, SLO, LT, LV	Winter wheat Triticum aestivum (TRZAW);	F	broadleaf weeds	Spray medium sprayer	Spring PL: BBCH 20-29 CZ: BBCH 21-29	a) — 1 b) — 1	n/a	a) — 0.4 b) — 0.4	a) — 0.12 b) — 0.12	200- 300	n/a	A
6	PL, CZ,	Sugar-beet	F	broadleaf	Spray	BBCH	a) — 1	n/a	a) — 0.4	a) — 0.12	200-	n/a	N

1	2	3	4	5	6	7	8	9	10	11	12	13	14
Use- No. ( <sup>e</sup> )	Member state(s)	Crop and/ or situa- tion  (crop destination /purpose of crop)	F, Fn, Fpn G, Gn, Gpn or I	Pests or Group of pests con- trolled  (additionally: developmental stages of the pest or pest group)	Application				Application rate			PHI (days)	Remarks:  e.g. g safen- er/synergist per ha ( <sup>g</sup> )
					Method / Kind	Timing/ Growth stage of crop & season	Max. number a) per use b) per crop/ season	Min. inter- val between applications (days)	kg or L product/hL a) max. rate per appl. b) max. total rate per crop/season	g or kg as/ha a) max. rate per appl. b) max. total rate per crop/season	Water L/ha  min/ max		
	RO, SLO, LT, LV	Beta-vul- garis (BEAVP)		weeds	medium sprayer	12–14	b) — 1		b) — 0.4	b) — 0.12	300		
7	PL, CZ, RO, SLO, LT, LV	Sugar beet Beta-vul- garis (BEAVP)	F	broadleaf weeds	Spray medium sprayer	BBCH 12–14	a) — 3 b) — 3	6–10	a) — 0.2 b) — 0.6	a) — 0.06 b) — 0.18	200- 300	n/a	N
<b>Interzonal uses (use as seed treatment, in greenhouses (or other closed places of plant production), as post harvest treatment or for treatment of empty storage rooms)</b>													
8													
9													
<b>Minor uses according to Article 51 (zonal uses)</b>													
10													
11													
<b>Minor uses according to Article 51 (interzonal uses)</b>													
12													
13													

<b>Remarks table heading:</b>	(a)	e.g. wettable powder (WP), emulsifiable concentrate (EC), granule (GR)	(d)	Select relevant
	(b)	Catalogue of pesticide formulation types and international coding system CropLife International Technical Monograph n°2, 6th Edition Revised May 2008	(e)	Use number(s) in accordance with the list of all intended GAPs in Part B, Section 0 should be given in column 1
	(c)	g/kg or g/l	(f)	No authorization possible for uses where the line is highlighted in grey, Use should be crossed out when the notifier no longer supports this use.



<b>Remarks columns:</b>	<p>1— Numeration necessary to allow references</p> <p>2— Use official codes/nomenclatures of EU Member States</p> <p>3— For crops, the EU and Codex classifications (both) should be used; when relevant, the use situation should be described (e.g. fumigation of a structure)</p> <p>4— F: professional field use, Fn: non-professional field use, Fpn: professional and non-professional field use, G: professional greenhouse use, Gn: non-professional greenhouse use, Gpn: professional and non-professional greenhouse use, I: indoor application</p> <p>5— Scientific names and EPPO-Codes of target pests/diseases/ weeds or, when relevant, the common names of the pest groups (e.g. biting and sucking insects, soil born insects, foliar fungi, weeds) and the developmental stages of the pests and pest groups at the moment of application must be named.</p> <p>6— Method, e.g. high volume spraying, low volume spraying, spreading, dusting, drench Kind, e.g. overall, broadcast, aerial spraying, row, individual plant, between the plants – type of equipment used must be indicated.</p> <p>7— Growth stage at first and 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</p> <p>8— The maximum number of application possible under practical conditions of use must be provided.</p> <p>9— Minimum interval (in days) between applications of the same product</p> <p>10— For specific uses other specifications might be possible, e.g.: g/m<sup>3</sup> in case of fumigation of empty rooms. See also EPPO-Guideline PP 1/239 Dose expression for plant protection products.</p> <p>11— The dimension (g, kg) must be clearly specified. (Maximum) dose of a.s. per treatment (usually g, kg or L product / ha).</p> <p>12— If water volume range depends on application equipments (e.g. ULVA or LVA) it should be mentioned under “application: method/kind”.</p> <p>13— PHI – minimum pre-harvest interval</p> <p>14— Remarks may include: Extent of use/economic importance/restrictions</p>													
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1	2	3	4	5	6	7	8				9			10	11			
GAP number (see part B.0)*	Crop and/or situation **	Zone	Product code	F, Fn, Fpn G, Gn, Gpn or I***	Pests or Group of pests controlled  (additionally: developmental stages of the pest or pest group)	Formulation		Application				Application rate			PHI (days)	Conclusion		
						Type	Conc. of as	Method / Kind	Growth stage of crop & season	number min max	interval between applications (min)	kg as/hL		water L/ha			kg as/ha	
												min	max	min				max
1	Winter oilseed rape Brassica napus, (BRSNW)	CEU	CHR/H/CPD 300 SL	F	broadleaf weeds	SL	300 g/L	Spray, medium sprayer	till BBCH 50	1	n/a	0.4	200-300	0.12	n/a	N Y****		
2	Winter oilseed rape Brassica napus, (BRSNW)	CEU	CHR/H/CPD 300 SL	F	broadleaf weeds	SL	300 g/L	Spray, medium sprayer	till BBCH 51	1	n/a	0.4	200-300	0.12	n/a	N Y****		
3	Winter oilseed rape Brassica napus, (BRSNW)	CEU	CHR/H/CPD 300 SL	F	annual and perennial broadleaf weeds	SL	300 g/L	Spray, medium sprayer	till BBCH 50	1	n/a	0.078+0.3 CHR/H/PCR* + CHR/H/CPD*	200-300	0.0234+0.09 CHR/H/PCR* + CHR/H/CPD*	n/a	N Y****		
4	Winter	CEU	CHR/H/CPD	F	annual and	SL	300	Spray	Autumn	1	n/a	0,078+0,3+1,5	200-300	0.0234+0.09+0.750	n/a	N		

	oilseed rape Brassica napus. (BRSNW)		300 SL		perennial broadleaf weeds		g/L	medium sprayer	BBCH 20-21			CHR/H/PCR* + CHR/H/CPD* + CHR/H/MTC*		CHR/H/PCR* + CHR/H/CPD* + CHR/H/MTC*		Y****
5	Winter wheat Triticum aestivum (TRZAW);	CEU	CHR/H/CPD 300 SL	F	broadleaf weeds	SL	300 g/L	Spray medium sprayer	Spring PL: BBCH 20-29 CZ: BBCH 21-29	1	n/a	0.4	200-300	0.12	n/a	A
6	Sugar beet Beta vulgaris (BEAVP)	CEU	CHR/H/CPD 300 SL	F	broadleaf weeds	SL	300 g/L	Spray medium sprayer	BBCH 12 - 14	1	n/a	0.4	200-300	0.12	n/a	N Y
7	Sugar beet Beta vulgaris (BEAVP)	CEU	CHR/H/CPD 300 SL	F	broadleaf weeds	SL	300 g/L	Spray medium sprayer	BBCH 12-14	3	6-10	0.2	200-300	0.06	n/a	N Y

\*. Use number(s) in accordance with the list of all intended GAPs in Part B, Section 0 should be given in column 1

\*\* Use also code numbers according to Annex I of Regulation (EU) No 396/2005

\*\*\* F: professional field use, Fn: non-professional field use, Fpn: professional and non-professional field use, G: professional greenhouse use, Gn: non-professional greenhouse use, Gpn: professional and non-professional greenhouse use, I: indoor application

\*\*\*\* Regarding missing data on residues in honey the decision on the possibility of authorizing the use on rapeseed can be made at the level of a Member State.

#### Explanation for column 11 "Conclusion"

A	Safe use
R	Further refinement and/or risk mitigation measures required
C	To be confirmed by cMS
N	No safe use

## 7.1.2 Summary of the evaluation

The preparation CHR/H/CPD 300 SL is composed of clopyralid.

**Table 7.1-2: Toxicological reference values for the dietary risk assessment of clopyralid**

Reference value	Source	Year	Value	Study relied upon	Safety factor
Clopyralid					
ADI	EFSA Journal 2018;16(7):5389	2018	0.15 mg/kg bw per day	rat, 2-year chronic toxicity and oncogenicity study	100
ARfD	EFSA Journal 2018;16(7):5389	2018	0.17 mg/kg bw	rabbit, developmental toxicity	300

### 7.1.2.1 Summary for clopyralid

**Table 7.1-3: Summary for clopyralid**

Use-No.*	Crop	Plant metabolism covered?	Sufficient residue trials?	PHI sufficiently supported?	Sample storage covered by stability data?	MRL compliance	Chronic risk for consumers identified?	Acute risk for consumers identified?
1, 2, 3, 4	Winter oilseed rape	Yes No	Yes	-	Yes	Yes	No	No
5	Winter wheat	Yes	Yes	-	Yes	Yes	No	No
6, 7	Sugar beet beetroots	Yes No	Yes	-	Yes	Yes	No	No

\* Use number(s) in accordance with the list of all intended GAPs in Part B, Section 0 should be given in column 1

### 7.1.2.2 Summary for CHR/H/CPD

**Table 7.1-4: Information on CHR/H/CPD 300 SL (KCA 6.8)**

Crop	PHI for CHR/H/CPD proposed by applicant	PHI/ Withholding period* sufficiently supported for clopyralid	PHI for CHR/H/CPD 300SL proposed by zRMS	zRMS Comments (if different PHI proposed)
Winter oilseed rape(spring)	PHIs are not required. They are determined by the growth stages of crops at application.	NR		
Winter oilseed rape(autumn)		NR		
Winter wheat		NR		
Sugar beet beetroots		NR		
Sugar beet beetroots		NR		

NR: not relevant

\* Purpose of withholding period to be specified

\*\* F: PHI is defined by the application stage at last treatment (time elapsing between last treatment and harvest of the crop).

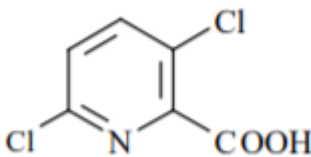
**Table 7.1-5: Waiting periods before planting succeeding crops**

Crop group	Overall waiting period proposed by zRMS
All crops	125 days after the initial application

## 7.2 Clopyralid

General data on clopyralid are summarized in the table below

**Table 7.2-1: General information on clopyralid**

Active substance (ISO Common Name)	Clopyralid
IUPAC	3,6-dichloropyridine-2-carboxylic acid
Chemical structure	
Molecular formula	C <sub>6</sub> H <sub>3</sub> Cl <sub>2</sub> NO <sub>2</sub>
Molar mass	191.96
Chemical group	3,6-dichloro-2-pyridinecarboxylic acid
Systemic	Yes
Company (ies)	Dow AgroSciences
Rapporteur Member State (RMS)	RMS - Finland Co-RMS - Poland
Approval status	<p>Approved  Date of approval (01/05/2007)  (COMMISSION DIRECTIVE 2006/74//EC - REGULATION (EU) No 540/2011)</p> <p>The renewal of approval  Date of approval 1 October 2021  COMMISSION IMPLEMENTING REGULATION (EU) 2021/1191 of 19 July 2021</p>
Restriction	<p>COMMISSION IMPLEMENTING REGULATION (EU) 2021/1191 of 19 July 2021</p> <p>Member States shall pay particular attention to:</p> <ul style="list-style-type: none"> <li>- the specification of the technical material as commercially manufactured;</li> <li>- the protection of operators, ensuring that conditions of use for operators include the application of adequate personal protective equipment;</li> </ul>

	<ul style="list-style-type: none"> <li>- possible presence of clopyralid residues in rotational crops;</li> <li>- the possible transfer of clopyralid residues via compost or manure of animals whose feed originates from treated areas, to avoid damage to susceptible crops;</li> <li>- the protection of groundwater under vulnerable conditions.</li> </ul>
Review Report	SANTE/10206/2021 Rev 1 20 May 2021
Current MRL regulation	COMMISSION REGULATION (EU) 2021/1807 of 13 October 2021
Peer review of MRLs according to Article 12 of Reg No 396/2005 EC performed	No
EFSA Journal : Conclusion on the peer review	Yes EFSA Journal 2018;16(7):5389
EFSA Journal: conclusion on article 12	No
Current MRL applications on intended uses	N/A – MRL already set

## 7.2.1 Stability of Residues (KCA 6.1)

### 7.2.1.1 Stability of residues during storage of samples

#### Available data

No new data submitted in the framework of this application.

### IIIA 8.1 Stability of Residues

Matrix	Characteristics of the matrix	Acceptable Maximum Storage duration	Reference
<b>Data relied on in EU</b>			
<b>Plant products</b>			
Maize forage/fodder	High water content	13 months	EFSA Journal 2018;16(7):5389 Clements, B, Bolton, A , (1996) RES93050.01; Foster, D.R., Blakeslee, B.A., Rutherford, B.S. DAS Study No. RES93050.01;1996
Pasture grass	High water content	17 months	EFSA Journal 2018;16(7):5389 Clements, B, Bolton, A , (1996) RES93050.01; Foster, D.R., Blakeslee, B.A., Rutherford, B.S. DAS Study No. RES93050.01;1996

Matrix	Characteristics of the matrix	Acceptable Maximum Storage duration	Reference
Maize ( corn grain)	High starch content	13 months	EFSA Journal 2018;16(7):5389 Clements, B, Bolton, A , (1996) RES93050.01; Foster, D.R., Blakeslee, B.A., Rutherford, B.S. DAS Study No. RES93050.01;1996
Oilseed rape (seed)	High oil content	24 months	EFSA Journal 2018;16(7):5389 Dial, E., Lindsay, D. 2006 DAS Study No. 020122.02
Animal products			
Bovine	Muscle	19 months	EFSA Journal 2018;16(7):5389 DAS Study No. 020120.01
Bovine	Liver Kidney Milk	19 months	EFSA Journal 2018;16(7):5389 DAS Study No. 020120.01
Hen	Eggs	19 months	EFSA Journal 2018;16(7):5389 DAS Study No. 020120.01
Bovine	Fat	24 months	EFSA Journal 2018;16(7):5389 DAS Study No. 120602;

According to EFSA Journal 2018;16(7):5389 stability of conjugates has not been tested, though clopyralid conjugates are major metabolites comprising up to 50 % of TRR depending on crop studied. It is assumed that conjugated clopyralid will be also stable.

#### 7.2.1.2 Stability of residues in sample extracts (KCA 6.1)

No further data is required.

#### 7.2.1.3 Nature of residue in primary crops (KCA 6.2.1)

The metabolism in primary crops presented during Annex I inclusion and renewal, covers use of CHR/H/CPD 300 SL. No new studies were necessary.

(Clopyralid RAR Volume 3 B7 Chapelo S., Caley 2002a; Chapelo S., Caley 2002b; Guo 1996)

Plant metabolism of clopyralid was studied in three crops: sugarbeet, oilseed rape, cabbage.

The extraction with caustic methanol employed in the cabbage study has led to cleavage of the conjugates and resulted in the presence of free clopyralid at maturity up to 92% and 99% total radioactive residue (TRR) in head and wrapper leaves, respectively. In the studies with oilseed rape and sugar beet, a first extraction was performed with acetonitrile/water and followed with a caustic extraction allowing for investigation of the presence of eventual conjugates. In sugar beet, clopyralid was initially the major residue in the plant (97% TRR at day 0 and 85% TRR at day 28). At maturity, it decreased to 51% TRR in the shoot and to 58% TRR in the root. A 'polar form of clopyralid' was observed in shoots and roots up to 37% TRR and 39% TRR, respectively, but only in the mature plant parts. In oilseed rape clopyralid

was present at 63% TRR in immature plant and at 32% and 43% TRR in mature straw and seed, respectively. A 'polar form of clopyralid' was reported to 32% and 28% TRR in mature straw and seed, respectively and an unknown metabolite B also referred to as 'clopyralid conjugates' to 29% and 18% TRR in mature straw and seed, respectively.

In the framework of the assessment of modification of the existing maximum residue levels for clopyralid in various commodities, a new metabolism study in wheat, representing cereals/grass crop group was submitted (EFSA Journal 2021;19(1):6389). EFSA concludes that for the intended uses in grass and cereals, the metabolic behaviour of clopyralid in these crops is addressed with the new metabolism study in wheat.

EFSA Journal 2021;19(1):6389: *Since the clarification of the unknown polar metabolite (called 'polar clopyralid') in mature sugar beet and oilseeds identified by the EU pesticides peer review was not sufficiently addressed under the current assessment, EFSA concludes that the proposed residue definitions are applicable only to cereals/grass crop group for which a new metabolism study was submitted under the current assessment and for which the data gap identified by the peer review is not relevant. For remaining crop groups, the data gap as identified by the EU pesticides peer review remains open.*

~~According to EFSA, the residue definition should be limited to cereals/grass only. Taking this into account, application on winter rape and sugar beet are not acceptable until the data gap is filled.~~

The intended uses on cereals are supported by the evaluated plant metabolism studies.

#### Authority's arrangements:

- in the case of clopyralid, assessment of residue data for the uses proposed by the Applicants, including, among others, on oilseeds, roots or tubers (crops other than representative crops assessed in RAR (2019) for the substance clopyralid) should be carried out in accordance with the general residue definition for clopyralid proposed by EFSA in the document EFSA Journal 2018;16(8):5389 - applies all administrative proceedings conducted by the Ministry of Agriculture and Rural Development (Article 33, Article 43, Article 40, Article 45, Article 51).

#### 7.2.1.4 Nature of residue in rotational crops (KCA 6.6.1)

##### Available data

No new data submitted in the framework of this application.

**Table 7.2-2: Summary of metabolism studies in rotational crops**

Crop group	Crop	Label position	Application and sampling details					Reference
			Method, F or G *	Rate (g a.s./ha)	Sowing intervals (DAT)	Harvest (BBCH)	Remarks	
EU data								
Leafy vegetables	Lettuce, Cabbage	pyridine	Spray, G	1 x 0.3 kg/ha to bare soil (30 days) 1 x 0.28 kg/ha to bare soil (125 and 319	125, 319 30	Immature BBCH 53 Mature BBCH 53		Yackovich, P. R. ; Lardie, T. S. ; Brink, D. L. , 1993, Study number: GH-C 2992; Yackovich, P.R.; Lardie

				days)				T.S.; Miller J.H., 1989, Study number: GH-C 2277;
<b>Root and tuber vegetables</b>	Turnip, Radish	pyridine	Spray, G	1 x 0.3 kg/ha to bare soil (30 days) 1 x 0.28 kg/ha to bare soil (125 and 319 days)	125, 319 30	53		Hall, L. R.; 2015; DAS Study No. 130733 to which is equivalent Rooney P., 2021, [14C]-
<b>Cereals</b>	Wheat	pyridine	Spray, G	1 x 0.3 kg/ha to bare soil (30 days) 1 x 0.28 kg/ha to bare soil (125 and 319 days)	30, 125, 319	Forage BBCH 43 Hay BBCH 71 Straw and grain BBCH 97		Clopyralid Metabolism in Rotational Crops FR/001647

\* Outdoor/field application (F) or glasshouse/protected/indoor application (G)

### Summary of plant metabolism studies reported in the EU

In plants, clopyralid is converted to at least one major conjugate that was readily hydrolysed in base to clopyralid. This result suggested that the conjugate was probably an ester formed by reaction with the carboxylic acid group in clopyralid. The nature of this residue, other than its hydrolysis to clopyralid, was not further investigated.

Another, usually minor pathway noted primarily in straw was binding to plant matrix. The majority of the bound residues in straw were solubilized by heating in 1 N NaOH, and this yielded several minor products that were characterized on the basis of distinctly different solubilities in MTBE, acid, and base.

### Conclusion on metabolism in rotational crops

The metabolism in rotational crops presented in Clopyralid, RAR, annex B, B.7 Residue, covers use of CHR/H/CPD 300 SL. No further studies are necessary.

#### 7.2.1.5 Nature of residues in processed commodities (KCA 6.5.1)

No new data submitted in the framework of this application.

**Table 7.2-4: Nature of the residues in processed commodities**

Conditions (Duration, Temperature, pH)	Identified compound(s) (%)	Reference
<b>EU data</b>		
<b>Pasteurisation</b> (20 minutes, 90°C, pH 4)	99.3 % of the initial clopyralid concentration	K. Hamnett; 2019; Study no: FR/001648 which is equivalent to Adusumilli, H. 2014; study no: 140574
<b>Baking, boiling, brewing</b> (60 minutes, 100°C, pH 5)	96.9 % of the initial clopyralid concentration	
<b>Sterilisation</b> (20 minutes, 120°C, pH 6)	97.1 % of the initial clopyralid concentration	



## Conclusion on nature of residues in processed commodities

The test compound clopyralid was stable under all conditions of high temperature hydrolysis for simulation of food processing. No changes proposed in residue definition on basis of hydrolysis test.

### 7.2.1.6 Conclusion on the nature of residues in commodities of plant origin (KCA 6.7.1)

**Table 7.2-5: Summary of the nature of residues in commodities of plant origin**

Endpoints	
Plant groups covered	Root crops(sugar beet), leafy crops( cabbage), Pulses/oilseeds(oilseed rape), cereals(wheat)
Rotational crops covered	Root/tuber crops(turnip, radish), leafy crops( lettuce, cabbage), Cereal(wheat),
Metabolism in rotational crops similar to metabolism in primary crops?	Yes
Processed commodities	a.s. is stable
Residue pattern in processed commodities similar to pattern in raw commodities?	Yes
Plant residue definition for monitoring	clopyralid common moiety (sum of clopyralid, its salts and conjugates expressed as clopyralid) – pending the outstanding clarification on the nature of “polar clopyralid” EFSA Journal 2018;16(7):5389 clopyralid (Reg. (EU) 2021/1807)
Plant residue definition for risk assessment	clopyralid common moiety (sum of clopyralid, its salts and conjugates expressed as clopyralid) – pending the outstanding clarification on the nature of “polar clopyralid” EFSA Journal 2018;16(7):5389  Applicable only for cereals/grass: clopyralid common moiety (sum of clopyralid, its salts and conjugates expressed as clopyralid) EFSA Journal 2021;19(1):6389
Conversion factor from enforcement to RA	N/A

\* If residue pattern in processed commodities is not similar to that in raw commodities

\*\* A more recent proposal by EFSA may be provided as additional information (EFSA RO XXXX).

\*\*\* If no EFSA proposal is available, a proposal should be made by the applicant/zRMS.

### 7.2.1.7 Nature of residues in livestock (KCA 6.2.2-6.2.5)

#### Available data

No new data submitted in the framework of this application.

**Table 7.2-6: Summary of animal metabolism studies**

Summary of animal metabolism studies								
Group	Species	Label position	No of animal	Application details		Sample details		Reference
				Rate (mg/kg bw/d)	Duration (days)	Commodity	Time of sampling	
EU data								
Ruminants	Caprine (goat)	[14C]Clopyralid labelled at two sites of the molecule	14	50.9 mg a.s./kg dry feed/day equivalent to 0.484 mg/kg bw per day	5	Milk	twice daily	A Nature of the Residue Study in the Ruminant with [14C]Clopyralid; ; Study No. 130202; 16 January 2015;
						Urine and faeces	daily	
						Tissues	at sacrifice	

Laying hen	Gallus domesticus	[14C]Clopyralid labelled at two sites of the molecule	N/A	11.4 mg a.s./kg feed per day, equivalent to 0.56-0.65 mg/kg bw per day	7	eggs	Once a day	Nature of the Residue Study in the Laying Hen with [14C]-Clopyralid; Study No. 130906; 20 November 2014;
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### Conclusion on metabolism in livestock

#### - poultry

It is concluded on basis of the laying hen study by (2014) that clopyralid metabolism is limited in laying hens. The majority of clopyralid is excreted unchanged.

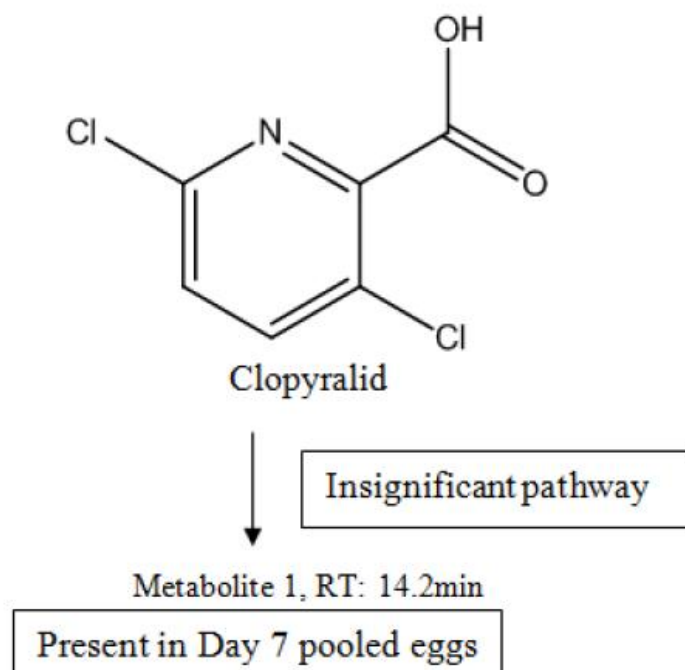
Identification rate in eggs varied from 52 to 72 %TRR on day 7, which is the last dosing day of the study. A deficiency of the study is 7 days was not long period enough to reach steady state. It is clear that on day 7 the levels of total radioactivity in eggs was still increasing.

Positive identification by HPLC tandem mass spectrometry was used for identification.

The study fulfils its objectives.

While a diminutive amount, 2.0% TRR and 0.0002 mg eq./kg is metabolized in eggs to an unidentified Metabolite 1.

A metabolic pathway is proposed below:



Clopyralid is minimally metabolized in laying hens.

Identification rate in eggs varied from 52 to 72 %TRR on day 7, which is the last dosing day of the study. A deficiency of the study is 7 days was not long period enough to reach steady state. It is clear that on day 7 the levels of total radioactivity in eggs was still increasing

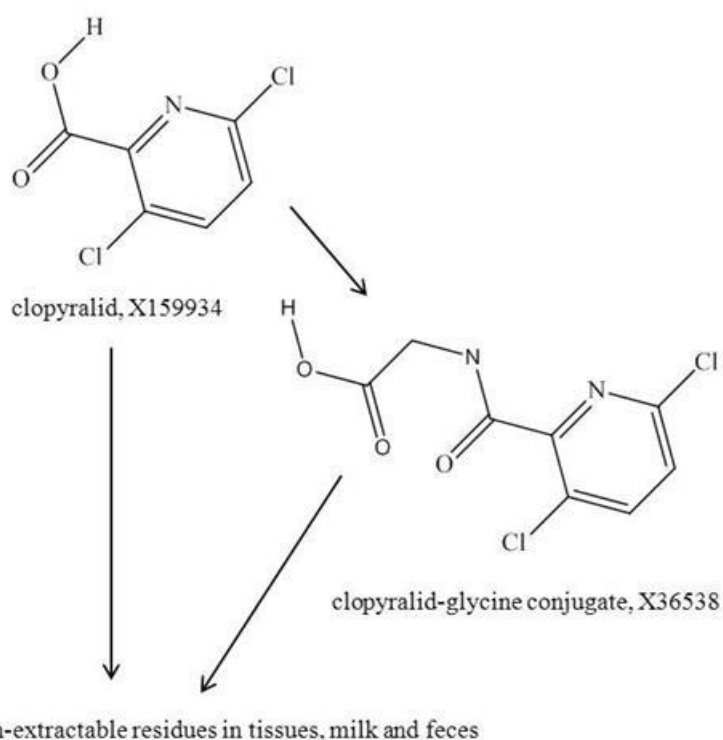
#### -Lactating ruminnats

In milk over 21% of TRR (corresponding to 0.002 mg eq/kg) was found as clopyralid-glycine conjugate (X36538).

Clopyralid comprised from 54% to over 70% of the TRR in milk, urine and faeces.

In the tissues unchanged clopyralid was the major residue along with minor amounts of conjugate X36538.

## Proposed metabolic profile of active substance in domestic animals.



### 7.2.1.8 Conclusion on the nature of residues in commodities of animal origin (KCA 6.7.1)

**Table 7.2-7: Summary on the nature of residues in commodities of animal origin**

	Endpoints
Animals covered	Goat, laying hen
Time needed to reach a plateau concentration	<p>- For clopyralid residues in milk dosing was once a day and the residues had already declined to low levels within one day. Any accumulating potential could not be demonstrated. Plateau was reached at day 1.</p> <p>- For eggs residue levels are still slightly increasing at the end of the experiment, i.e. after 7 days of dosing, but a plateau can be assumed at day 7.</p>
Animal residue definition for monitoring	clopyralid and its salts (EFSA Journal 2018;16(7):5389) clopyralid (Reg. (EU) 2021/1807)
Animal residue definition for risk assessment	clopyralid common moiety (sum of clopyralid, its salts and glycine conjugates expressed as clopyralid) (EFSA Journal 2018;16(7):5389)
Conversion factor	The conversion factor monitoring / risk assessment is only relevant for milk and is based on the new ruminant metabolism study as 1.3. (EFSA Journal 2018;16(7):5389)
Metabolism in rat and ruminant similar	Yes (EFSA Journal 2018;16(7):5389)
Fat soluble residue	No (EFSA Journal 2018;16(7):5389)

\* A more recent proposal by EFSA may be provided as additional information (EFSA RO XXXX)

\*\* If no EFSA proposal is available, a proposal should be made by the applicant/zRMS.

\*\*\* If metabolism in rat and ruminant are not similar

## 7.2.2 Magnitude of residues in plants (KCA 6.3)

### 7.2.2.1 Summary of European data and new data supporting the intended uses

March 2024  
The new residue studies are accepted

Commodity	Source	Residue zone (N-EU, S-EU, EU, outside EU)	Evaluation GAP Residue levels (mg/kg) E = according to enforcement residue definition RA = according to risk assessment residue definition		Substrate	STMR (mg/kg)	HR (mg/kg)	Unrounded OECD calculator MRL (mg/kg)	Current EU MRL (mg/kg) <small>Annex I</small>	MRL compliance
Sugar beet	DAR_05_vol3_B7	N-EU	Trials GAP: clopyralid 100 ga.s./ha + 200 g a.s./ha outdoor BBCH 14	1x0.36, 1x0.34, 1x0.29, 1x0.41, 1x0.35, 1x0.56, 1x0.21, 1x0.17, 1x0.12, 1x0.80,	Roots	0.345	0.8	-	1mg/kg	Yes
				1x0.46, 1x0.57, 1x0.23, 1x1.05, 1x0.36, 1x0.47, 1x0.14, 1x0.47, 1x0.13, 1x0.62	Tops	0.465	1.050	-		N/A
				1x0.42, 1x0.59, 1x0.12, 1x0.46	Whole plant	0.44	0.590	-		N/A
	C. Lefebvre, 2023 Study No. C2105	N-EU	Trials GAP: Clopyralid 157.5 g a.s./ha outdoor BBCH 14	0.04		Roots	0.050	0.150	0.261	Yes
	C. Lefebvre, 2023		Trials GAP: Clopyralid 161 g a.s./ha	0.15						

	Study No. C2127	outdoor BBCH 14							
	C. Lefebvre, 2023 Study No. C2128	Trials GAP: Clopyralid 136.7 g a.s./ha outdoor BBCH 14	0.14						
	C. Lefebvre, 2023 Study No. C2129	Trials GAP: Clopyralid 150 g a.s./ha outdoor BBCH 14	0.09						
	C. Lefebvre, 2023 Study No. C2130	Trials GAP: Clopyralid 165.8 g a.s./ha outdoor BBCH 14	0.06						
	C. Lefebvre, 2023 Study No. C2131	Trials GAP: Clopyralid 148 g a.s./ha outdoor BBCH 14	< LOQ						
	C. Lefebvre, 2023 Study No. C2132	Trials GAP: Clopyralid 155 g a.s./ha outdoor BBCH 14-16	0.05						
	C. Lefebvre, 2023 Study No. C2133	Trials GAP: Clopyralid 153.3 g a.s./ha outdoor BBCH 14	0.04						
	C. Lefebvre, 2023 Study No. C2134	Trials GAP: Clopyralid 142.9 g a.s./ha outdoor BBCH 14	0.04						
	C. Lefebvre, 2023 Study No. C2105	Trials GAP: Clopyralid 157.5 g a.s./ha outdoor BBCH 14	0.08	Leaves with tops	0.070	0.25	0.402		N/A
	C. Lefebvre, 2023 Study No. C2127	Trials GAP: Clopyralid 161 g a.s./ha outdoor BBCH 14	0.20						
	C. Lefebvre, 2023 Study	Trials GAP: Clopyralid 136.7 g a.s./ha	0.25						

	No. C2128		outdoor BBCH 14							
	C. Lefebvre, 2023 Study No. C2129		Trials GAP: Clopyralid 150 g a.s./ha outdoor BBCH 14	0.09						
	C. Lefebvre, 2023 Study No. C2130		Trials GAP: Clopyralid 165.8 g a.s./ha outdoor BBCH 14	0.07						
	C. Lefebvre, 2023 Study No. C2131		Trials GAP: Clopyralid 148 g a.s./ha outdoor BBCH 14	0.01						
	C. Lefebvre, 2023 Study No. C2132		Trials GAP: Clopyralid 155 g a.s./ha outdoor BBCH 14-16	0.07						
	C. Lefebvre, 2023 Study No. C2133		Trials GAP: Clopyralid 153.3 g a.s./ha outdoor BBCH 14	0.06						
	C. Lefebvre, 2023 Study No. C2134		Trials GAP: Clopyralid 142.9 g a.s./ha outdoor BBCH 14	0.06						
Oilseed rape	DAR_05_vol3_B7	N-EU	Trials GAP: clopyralid 1x 0.1 kg a.s./ha + 1 x 0.2 kg a.s./ha outdoor BBCH 51	1x 0.03, 1x0.05, 2x0.02, 1x0.10, 1x0.04, 1x0.01, <0.003	seed	0.025	0.1	-	0.5mg/kg	Yes
				1x1.40, 1x0.30, 1x0.13, 1x<0.01	straw	0.215	1.4	-		N/A
				1x0.59, 1x 1.74, 1x1.48,	Whole plant	1.48	1.74	-		N/A
				1x0.02, 1x0.54, 1x0.28	Rest of plant	0.28	0.54	-		N/A
	E. Thomas - Delille, 2023 Study		Trials GAP: Clopyralid 122.7 g a.s./ha outdoor BBCH 51	0.02	Seed	0.015	0.040	0.079		Yes

	No. C2104									
	E. Thomas - Delille, 2023 Study No. C2120		Trials GAP: Clopyralid 124 g a.s./ha outdoor BBCH 51	NDR						
	E. Thomas - Delille, 2023 Study No. C2121		Trials GAP: Clopyralid 113.6 g a.s./ha outdoor BBCH 51	0.04						
	E. Thomas - Delille, 2023 Study No. C2122* *		Trials GAP: Clopyralid 118.4 g a.s./ha outdoor BBCH 52- 53	0.04						
	E. Thomas - Delille, 2023 Study No. C2123* *		Trials GAP: Clopyralid 115.2 g a.s./ha outdoor BBCH 51	<LOQ						
	E. Thomas - Delille, 2023 Study No. C2124* *		Trials GAP: Clopyralid 116.3 g a.s./ha outdoor BBCH 51	0.03						
	E. Thomas - Delille, 2023 Study No. C2125* *		Trials GAP: Clopyralid 128.9 g a.s./ha outdoor BBCH 51	<LOQ						
	E. Thomas - Delille, 2023 Study No. C2126* *		Trials GAP: Clopyralid 116 g a.s./ha outdoor BBCH 51	0.01						

Cereals	<i>DAR_05_vol3_B7</i>	N-EU	Trials GAP: clopyralid 0.150kg/ha, outdoor BBCH 39	1x0.93, 1x0.73, 1x0.23, 1x0.07, 1x0.79, 1x1.11, 1x1.06, 1x1.26, 1x0.38, 1x0.24, 1x0.82, 1x0.95, 1x0.14, 1x0.37, 1x0.61, 1x0.34, 1x0.47	Grain	0.61	1.26	-	3mg/kg	Yes	
	1x0.12, 1x0.32, 1x0.63, 1x0.43, 1x0.33, 1x0.58, 1x0.81, 1x0.17, 1x0.32, 1x0.28, 1x0.50, 1x0.40, 1x1.08, 1x1.05, 1x0.87, 1x0.31			Straw	0.415	1.08	-	N/A			
	1x1.16, 1x1.06, 1x1.62, 1x1.15, 1x0.31, 1x1.57, 1x0.46, 1x0.89			Whole plant	1.105	1.62	-	N/A			
	<i>E. Schneider, 2023 C2114</i>			Trials GAP: clopyralid 118.7 g/ha, outdoor BBCH 29	0.45	Grain	0.405	0.85		1.451	Yes
	<i>E. Schneider, 2023 C2115</i>			Trials GAP: clopyralid 115.7 g/ha, outdoor BBCH 29	0.80						
	<i>E. Schneider, 2023 C2116</i>			Trials GAP: clopyralid 118.4 g/ha, outdoor BBCH 29	0.54						
	<i>E. Schneider, 2023 C2117</i>			Trials GAP: clopyralid 122.7 g/ha, outdoor BBCH 29	0.27						
	<i>E.</i>			Trials GAP:	0.34						



	<i>Schneider</i> , 2023 C2103		clopyralid 130.0 g/ha, outdoor BBCH 29							
	<i>E. Schneider</i> 2023 C2111		Trials GAP: clopyralid 123.2 g/ha, outdoor BBCH 29	0.36						
	<i>E. Schneider</i> 2023 C2112		Trials GAP: clopyralid 128.7 g/ha, outdoor BBCH 29	0.85						
	<i>E. Schneider</i> 2023 C2118		Trials GAP: clopyralid 124 g/ha, outdoor BBCH 29	0.26						
	<i>E. Schneider</i> 2023 C2114		Trials GAP: clopyralid 118.7 g/ha, outdoor BBCH 29	0.52	Straw	0.645	0.93	1.90		Yes
	<i>E. Schneider</i> 2023 C2115		Trials GAP: clopyralid 115.7 g/ha, outdoor BBCH 29	0.81						
	<i>E. Schneider</i> 2023 C2116		Trials GAP: clopyralid 118.4 g/ha, outdoor BBCH 29	0.76						
	<i>E. Schneider</i> 2023 C2117		Trials GAP: clopyralid 122.7 g/ha, outdoor BBCH 29	0.59						
	<i>E. Schneider</i> 2023 C2103		Trials GAP: clopyralid 130.0 g/ha, outdoor BBCH 29	0.27						
	<i>E. Schneider</i> 2023 C2111		Trials GAP: clopyralid 123.2 g/ha, outdoor BBCH 29	0.70						
	<i>E. Schneider</i> 2023 C2112		Trials GAP: clopyralid 128.7 g/ha, outdoor	0.93						

			BBCH 29							
	<i>E. Schneider, 2023 C2118</i>		Trials GAP: clopyralid 124 g/ha, outdoor BBCH 29	0.50						

\* Source of EU MRL: COMMISSION REGULATION (EU) 2021/1807

\*\* Studies performed CHR/H/CPD 300 SL with the adjuvant Asystem +. The results resulting from these studies are comparable with results from studies on oilseed rape conducted without the adjuvant, therefore applicant provided sufficient data to support the intended use of CHR/H/CPD 300 SL with Adjuvant+ (autumn use).

## Conclusions

According to the available data, the intended use in sugar beets, beetroots, oilseed rape and winter wheat is considered acceptable. The data submitted show that no exceedance of the MRL will occur. The uses are considered acceptable.

### 7.2.3 Magnitude of residues in livestock

#### 7.2.3.1 Dietary burden calculation

March 2024

New Dietary Burden calculations were performed, taking into account STMR and HR values for Sugar beet, Wheat and Oilseed rape from new residues trials on Faworyt 300 SL / CHR/H/CPD 300 SL. The new calculation results do not change the conclusions.

**Table 7.2-9: Input values for the dietary burden calculation (considering the uses authorized within the zone and the uses under consideration)**

Feed Commodity	Median dietary burden		Maximum dietary burden	
	Input value (mg/kg)	Comment	Input value (mg/kg)	Comment
Residues expressed as Clopyralid				
Beet mangel, fodder	0.465	STMR (please refer to Table 7.2-8)	1.05	HR (please refer to Table 7.2-8)
Beet sugar, tops	0.465	STMR (please refer to Table 7.2-8)	1.05	HR (please refer to Table 7.2-8)
Beet sugar, roots	0.345	STMR (please refer to Table 7.2-8)	0.8	HR (please refer to Table 7.2-8)
Beet sugar, ensiled pulp	6.21	STMR x default PF	N/A	N/A
Beet sugar, molasses	9.66	STMR x default PF	N/A	N/A
Beet sugar, dried pulp	6.21	STMR x default PF	N/A	N/A
Beet mangel, fodder	0.070	STMR (please refer to Table 7.2-8)	0.25	HR (please refer to Table 7.2-8)
Beet sugar, tops	0.070	STMR (please refer to Table 7.2-8)	0.25	HR (please refer to Table 7.2-8)
Beet sugar, roots	0.050	STMR (please refer to Table 7.2-8)	0.150	HR (please refer to Table 7.2-8)
Beet sugar, ensiled pulp	0.15	STMR x default PF	N/A	N/A
Beet sugar, molasses	1.4	STMR x default PF	N/A	N/A
Beet sugar, dried pulp	0.9	STMR x default PF	N/A	N/A
Wheat, grain	0.61 0.41	STMR (please refer to Table 7.2-8)	1.26	HR (please refer to Table 7.2-8)
Wheat, straw	0.415 0.65	STMR (please refer to Table 7.2-8)	1.08	HR (please refer to Table 7.2-8)
Canola, meal	0.05 0.03	STMRx default PF	N/A	N/A
Rape, meal	0.05 0.03	STMRx default PF	N/A	N/A
Distiller's grain, dried	2.01 1.34	STMRx default PF	N/A	N/A

Feed Commodity	Median dietary burden		Maximum dietary burden	
	Input value (mg/kg)	Comment	Input value (mg/kg)	Comment
Wheat gluten, meal	1.10 0.73	STMRxdefault PF	N/A	N/A
Wheat, milled by-pdts	4.27 2.84	STMRxdefault PF	N/A	N/A
Wheat forage	0.65	STMR	N/A	N/A
Wheat hay	2.28	STMRxdefault PF	N/A	N/A

New Dietary Burden calculations were performed, taking into account STMR and HR values from residues trials on CHR/H/CPD 300 SL. New calculations were presented below in Animal model 2017.

**Table 7.2-10: Results of the dietary burden calculation**

Animal burden calculation							clopyralid				
According to: "OECD Guidance Document, Series on testing and assessment No 64 and Series on pesticides No 32" and "OECD Guidance Document on Residues in livestock, Series on Pesticides No 73"											
Maximum Intake	Cattle						Sheep				
	Beef			Dairy			Ram/Ewe			Lamb	
(mg/kg bw/d)	0.0984	mg/kg bw/d	%	0.1827	mg/kg bw/d	%	0.1337	mg/kg bw/d	%	0.1704	mg/kg bw/d
Contributor 1	Beet, mangel	fodder	30	Beet, mangel	fodder	25	Beet, sugar	dried pulp	40	Beet, sugar	dried pulp
Contributor 2	Beet, sugar	ensiled pulp	25	Beet, sugar	ensiled pulp	40	Beet, sugar	tops	20	Beet, sugar	tops
Contributor 3	Wheat	grain	40	Wheat	grain	35	Wheat	grain	40	Wheat	grain
Contributor 4											
Median intake	0.0703	mg/kg bw/d		0.1452	mg/kg bw/d		0.1167	mg/kg bw/d		0.1488	mg/kg bw/d
Maximum Intake	Swine						Intakes >0.004 mg/kg bw/d are highlighted				
	Breeding			Finishing							
(mg/kg bw/d)	0.086	mg/kg bw/d	%	0.083	mg/kg bw/d	%					
Contributor 1	Beet, mangel	fodder	15	Wheat	milled bypds	50					
Contributor 2	Wheat	milled bypds	50	Wheat	grain	50					
Contributor 3	Wheat	grain	35								
Contributor 4											
Median intake	0.072	mg/kg bw/d		0.083	mg/kg bw/d						
Maximum Intake	Poultry										
	Broiler			Layer			Turkey				
(mg/kg bw/d)	0.102	mg/kg bw/d	%	0.115	mg/kg bw/d	%	0.094	mg/kg bw/d	%		
Contributor 1	Wheat	milled bypds	20	Wheat	milled bypds	20	Wheat	milled bypds	20		
Contributor 2	Wheat	grain	70	Beet, sugar	tops	5	Wheat	grain	50		
Contributor 3				Wheat	grain	70					
Contributor 4											
Median intake	0.102	mg/kg bw		0.106	mg/kg bw		0.094	mg/kg bw			
Intakes expressed on the dry mater basis (mg/kg DM)											
mg/kg DM	Cattle			Sheep			Swine				
	Beef	Dairy		Ram/Ewe	Lamb		Breeding	Finishing			
Maximum	4.0992	4.75		4.01	4.01		3.72	2.77			
Median	2.9292	3.77		3.50	3.50		3.13	2.77			
	Poultry			Intake >0.1 mg/kg DM in red characters							
	Broiler	Layer	Turkey								
Maximum	1.45	1.68	1.31								
Median	1.45	1.55	1.31								

**zRMS calculation** (considering the intended uses):

Relevant groups	Dietary burden expressed in				Most critical diet (a)	Most critical commodity (b)		Trigger exceeded (Yes/No)			
	mg/kg bw per day							0.004			
	mg/kg DM										
	Median	Maximum	Median	Maximum				mg/kg bw			
Cattle (all diets)	0,137	0,167	3,57	4,34	Dairy cattle	Beet, sugar	ensiled pulp	Yes			
Cattle (dairy only)	0,137	0,167	3,57	4,34	Dairy cattle	Beet, sugar	ensiled pulp	Yes			
Sheep (all diets)	0,149	0,170	3,50	4,01	Lamb	Beet, sugar	dried pulp	Yes			
Sheep (ewe only)	0,087	0,134	2,62	4,01	Ram/Ewe	Beet, sugar	dried pulp	Yes			
Swine (all diets)	0,083	0,083	2,90	3,16	Swine (finishing)	Wheat	milled bypdts	Yes			
Poultry (all diets)	0,106	0,115	1,55	1,68	Poultry layer	Wheat	milled bypdts	Yes			
Poultry (layer only)	0,106	0,115	1,55	1,68	Poultry layer	Wheat	milled bypdts	Yes			

New Dietary Burden calculations were performed, taking into account STMR and HR values for Sugar beet, Wheat and Oilseed rape from new residues trials on Faworyt 300 SL / CHR/H/CPD 300 SL. New calculations were presented below in Animal model 2017.

Animal burden calculation							clopyralid								
According to:		"OECD Guidance Document, Series on testing and assessment No 64 and Series on pesticides No 32" and "OECD Guidance Document on Residues in livestock, Series on Pesticides No 73"													
Maximum Intake	Cattle						Sheep								
	Beef			Dairy			Ram/Ewe			Lamb					
	500 kg 12 kg			650 kg 25 kg			75 kg 2.5 kg			40 kg 1.7 kg					
(mg/kg bw/d)	0.0780	mg/kg bw/d	%	0.1115	mg/kg bw/d	%	0.0956	mg/kg bw/d	%	0.1198	mg/kg bw/d	%			
Contributor 1	Beet, mangel	fodder	30	Beet, mangel	fodder	25	Wheat	forage	40	Wheat	forage	30			
Contributor 2	Wheat	milled bypdt	30	Wheat	milled bypdt	30	Wheat	milled bypdt	40	Wheat	milled bypdt	50			
Contributor 3	Wheat	grain	40	Wheat	grain	40	Wheat	grain	20	Wheat	grain	20			
Contributor 4															
Median Intake	0.0400	mg/kg bw/d		0.0643	mg/kg bw/d		0.0807	mg/kg bw/d		0.1055	mg/kg bw/d				
Maximum Intake	Swine						Intakes >0.004 mg/kg bw/d are highlighted								
	Breeding			Finishing											
	260 kg 6 kg			100 kg 3 kg											
(mg/kg bw/d)	0.065	mg/kg bw/d	%	0.055	mg/kg bw/d	%									
Contributor 1	Beet, mangel	fodder	15	Wheat	milled bypdt	50									
Contributor 2	Wheat	milled bypdt	50	Wheat	grain	50									
Contributor 3	Wheat	grain	35												
Contributor 4															
Median Intake	0.052	mg/kg bw/d		0.055	mg/kg bw/d										
Maximum Intake	Poultry														
	Broiler			Layer									Turkey		
	1.7 kg 0.12 kg			1.9 kg 0.13 kg									7 kg 0.5 kg		
(mg/kg bw/d)	0.068	mg/kg bw/d	%	0.091	mg/kg bw/d	%							0.062	mg/kg bw/d	%
Contributor 1	Wheat	milled bypdt	20	Wheat	forage	10							Wheat	milled bypdt	20
Contributor 2	Wheat	grain	70	Wheat	milled bypdt	20							Wheat	grain	50
Contributor 3				Wheat	grain	70									
Contributor 4															
Median Intake	0.068	mg/kg bw		0.084	mg/kg bw								0.062	mg/kg bw	
Intakes expressed on the dry mater basis (mg/kg DM)															
mg/kg DM	Cattle				Sheep				Swine						
	Beef		Dairy		Ram/Ewe		Lamb		Breeding		Finishing				
Maximum	3.2405		2.90		2.87		2.82		2.82		1.84				
Median	1.6685		1.67		2.42		2.48		2.27		1.84				
	Poultry				Intake >0.1 mg/kg DM in red characters										
	Broiler		Layer										Turkey		
Maximum	0.96		1.33										0.87		
Median	0.96		1.22										0.87		
Relevant groups	Dietary burden expressed in				Most critical diet (a)	Most critical commodity (b)		Trigger exceeded (Yes/No)	Previous assessment						
	mg/kg bw per day		mg/kg DM												
	Median	Maximum	Median	Maximum											
Cattle (all diets)	0.064	0.111	1.67	3.25	Dairy cattle	Beet, mangel	fodder	Yes							
Cattle (dairy only)	0.064	0.111	1.67	2.90	Dairy cattle	Beet, mangel	fodder	Yes							
Sheep (all diets)	0.105	0.120	2.48	2.87	Lamb	Wheat	forage	Yes							
Sheep (ewe only)	0.081	0.096	2.42	2.87	Ram/Ewe	Wheat	forage	Yes							
Swine (all diets)	0.055	0.065	2.27	2.82	Swine (breeding)	Beet, mangel	fodder	Yes							
Poultry (all diets)	0.084	0.091	1.22	1.33	Poultry layer	Wheat	forage	Yes							
Poultry (layer only)	0.084	0.091	1.22	1.33	Poultry layer	Wheat	forage	Yes							
(a): When several diets are relevant (e.g. cattle, sheep and poultry "all diets"), the most critical diet is identified from the maximum dietary burdens expressed as "mg/kg bw per day"															
(b): The most critical commodity is the major contributor identified from the maximum dietary burden expressed as "mg/kg bw per day".															

## Livestock feeding studies (KCA 6.4.1-6.4.3)

According to EFSA Journal 2018;16(7):5389 new livestock feeding studies are performed during Annex I inclusion and renewal. No new livestock studies feeding studies are necessary.

OECD Guideline 503 and SANCO/11187/2013 rev. 3 (fish)	Animal	Dose (mg/kg bw/d)	Duration (days)	N rate/comment
Animals covered	Laying hen	11.4 mg a.s./kg feed per day, equivalent to 0.56-0.65 mg/kg bw per day	7	N rates can be established only once HR and STMR for cereal straw and grass from valid residue trials are available.
	Goat/Cow	50.9 mg a.s./kg dry feed/day equivalent to 0.484 mg/kg bw per day	5	N rates can be established only once HR and STMR for cereal straw and grass from valid residue trials are available.
	Pig			Not considered necessary.
	Fish			No studies submitted.
	In milk over 21% of TRR (corresponding to 0.002 mg eq/kg) was found as clopyralid-glycine conjugate (X36538). Clopyralid comprised from 54% to over 70% of the TRR in milk, urine and faeces. In the tissues unchanged clopyralid was the major residue along with minor amounts of conjugate X36538.			

Time needed to reach a plateau concentration in milk and eggs (days)	<p>For clopyralid residues in milk dosing was once a day and the residues had already declined to low levels within one day. Any accumulating potential could not be demonstrated. Plateau was reached at day 1.</p> <p>For eggs residue levels are still slightly increasing at the end of the experiment, i.e. after 7 days of dosing, but a plateau can be assumed at day 7.</p>
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## 7.2.4 Magnitude of residues in processed commodities (Industrial Processing and/or Household Preparation) (KCA 6.5.2-6.5.3)

Data/information on processing studies on wheat was reviewed during the renewal of approval of active substance(s) and were considered acceptable. No new study is necessary.

Data/information on processing studies on sugar beet were reviewed during the Annex I inclusion process and was considered to be acceptable and no further studies have been generated.

### 7.2.4.1 Available data for all crops under consideration

Please refer to Clopyralid RAR (Section B.7) (Devine, H.C., 2006, Study report no. GHE-P-11274 to which are equivalent Tim White, 2021, study codes: S19-01810, S20-04937)

Crop (RAC)/Edible part or Crop (RAC)/Processed product	Number of studies <sup>(a)</sup>	Processing Factor (PF)		Conversion Factor (CF <sub>p</sub> ) for RA <sup>(b)</sup>
		Individual values	Median PF	
Representative uses (row to be deleted if not relevant)				
Wheat / bran	4	3.5, 4.3, 6.1, 10.4	6.1 / 5.2	N/A
Wheat / white flour	4	0.1, 0.2, 0.3, 0.6	0.3 / 0.3	N/A
Wheat / wholemeal flour	2	0.8, 1.2	1 / 1	N/A
Wheat / germ	2	2.3, 4.3	3.3	N/A
Wheat / white bread	2	0.1, 0.1	0.1 / 0.1	N/A
Wheat / wholemeal bread	2	0.5, 0.6	0.6 / 0.6	N/A
Barley / malt sprouts	2	0.2, 0.2	0.2 / 0.2	N/A
Barley / brewing malt	2	0.6, 0.7	0.7 / 0.7	N/A
Barley / spent grains and flocs	2	0.1, 0.2	0.2 / 0.2	N/A
Barley / brewer's yeast	2	0.1, 0.1	0.1 / 0.1	N/A
Barley / beer	2	0.1, 0.1	0.1 / 0.1	N/A

<sup>(a)</sup>: Studies with residues in the RAC at or close to the LOQ should be disregarded (unless concentration)

<sup>(b)</sup>: When the residue definition for risk assessment differs from the residue definition for monitoring

#### 7.2.4.2 Conclusion on processing studies

Results of residue in processed commodities may therefore be used in order to predict the residue behaviour of clopyralid after usage of Major 300SL.

#### 7.2.5 Magnitude of residues in representative succeeding crops

According to EFSA Journal 2018;16(7):5389 residues in succeeding crops were reviewed during the Annex I inclusion and renewal process and were considered to be acceptable and no further data have been generated.

Crops under evaluation are expected to be grown in rotation.

##### Residues in succeeding crops (Regulation (EU) N° 283/2013, Annex Part A, point 6.6.2)

###### Confined rotational crop study

(Quantitative aspect)

OECD Guideline 502

In rotational crop intervals majority of the residue identified was clopyralid conjugates (up to 81%TRR) most abundant residue at all PBIs. Unconjugated clopyralid correspond from 10 to 50 %TRR. Clopyralid taken up by the plants as glucose conjugate of clopyralid

###### Field rotational crop study

OECD Guideline 504

Data gap: Rotational crop field trials according to current guidelines should be submitted as residues of free and conjugated parent were found in all plant parts at PHI 30.

**zRMS:** According to the available data following label restriction is proposed: not to use clopyralid on the same field for 125 days after the initial application regardless of the crop grown (see EFSA Journal 2021;19(1):6389).

EFSA Journal 2021;19(1):6389:

Residues in rotational and succeeding crops expected based on confined rotational crop study?	Yes	In rotational crop majority of the residue identified at PHI 30 days was clopyralid conjugates (up to 81% TRR) and unconjugated clopyralid (10 – 50% TRR) in all crop parts except radish roots. In total, 81–99% of the extractable radioactivity was attributed to clopyralid and its conjugate.
Residues in rotational and succeeding crops expected based on field rotational crop study?	Not provided	Rotational crop field trials according to current guidelines are requested as residues of free and conjugated parent were found in all plant parts at PHI 30. Until these studies become available EFSA suggests to risk managers as risk mitigation measure to label clopyralid containing products with the restriction not



		to use clopyralid on the same field for 125 days after the initial application regardless of the crop grown.
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### 7.2.5.1 Field rotational crop studies (KCA 6.6.2)

No new data submitted in the framework of this application.

### 7.2.6 Other / special studies (KCA6.10, 6.10.1)

The available data for the active substance sufficiently address aspects of the residue situation that might arise from the use of CHR/H/CPD 300 SL. Therefore, other special studies are not needed.

05.2024	III commenting round
<p>As follows from comment contained in <i>Reporting table Part A and B for Major 300 SL after III commenting round</i>, one of member state does not agree to authorization of the intended use (oilseed rape – melliferous crop) until the new MRL has been set for honey. zRMS considers that the decision on the possibility of authorizing the use on rapeseed can be made at the level of a Member State.</p> <p>Taking into account the date of submission of the documents and the date of application of the product shown in the GAP Table, the missing data may be required after registration of the plant protection product. In accordance with the arrangements in place in Poland, Poland agrees to such intended use provided that the study is performed after registration (post-registration requirement).</p>	

### 7.2.7 Estimation of exposure through diet and other means (KCA 6.9)

March 2024
New consumer calculations were performed considering STMR/HR values from newly submitted residue studies on Sugar beet., Oilseed rape and Wheat. The new calculation results do not change the conclusions.

The available data for the active substance sufficiently address aspects of the residue situation that might arise from the use of CHR/H/CPD. Therefore, other special studies are not needed.

### 7.2.7.1 Input values for the consumer risk assessment

Table 7.2-12: Input values for the consumer risk assessment

Commodity	Chronic risk assessment		Acute risk assessment	
	Input value (mg/kg)	Comment	Input value (mg/kg)	Comment
Sugar beet(root)/sugar, beetroots	1	COMMISSION REGULATION (EU) 2021/1807	1	COMMISSION REGULATION (EU) 2021/1807
Rapeseeds/oil	0.5	COMMISSION REGULATION (EU) 2021/1807	0.5	COMMISSION REGULATION (EU) 2021/1807
Wheat/bread (wholemeal); Wheat/bread/pizza; Wheat/pasta; Wheat/ milling (flour);	3	COMMISSION REGULATION (EU) 2021/1807	3	COMMISSION REGULATION (EU) 2021/1807

Commodity	Chronic risk assessment		Acute risk assessment	
	Input value (mg/kg)	Comment	Input value (mg/kg)	Comment
Wheat/ milling(wholemeal) -baking				

New consumer calculations were performed considering STMR/HR values from newly submitted residue studies on Sugar beet., Oilseed rape and Wheat.

### 7.2.7.2 Conclusion on consumer risk assessment


Extensive calculation sheets are presented in Appendix 3.

**Table 7.2-13: Consumer risk assessment**

Clopyralid		
<b>ADI</b>	0.15 mg/kg bw per day	
<b>TMDI (% ADI) according to EFSA PRIMo rev. 3.1</b>	15% (based on GEMS/Food) 14% (based on NL child Diet)	
<b>IEDI (% ADI) according to EFSA PRIMo rev. 3.1</b>	4% (based on NL child Diet) 2% (based on GEMS/Food G06)	
<b>ARfD</b>	0.17 mg/kg bw per day	
<b>IESTI (% ARfD) according to EFSA PRIMo rev. 3.1</b>	Processed	21% (sugar beet, root, sugar) 26% Beetroots / boiled (children)  3 % Wheat (children) 5% Beetroots (children)
	unprocessed	6% (wheat, children) 34% beetroots (children)  4% Beetroots / boiled (children) 3% Sugar beets (root) (children) 3% Wheat/ milling flour(children) 1% Wheat / milling wholemeal (children)

The proposed use of clopyralid in the formulation CHR/H/CPD 300 SL do not represent unacceptable acute and chronic risks for the consumer.

## Revision of the assessment taking into account the application to *Beta vulgaris*

 European Food Safety Authority EFSA PRIMo revision 3.1: 2019/03/19		<b>clopyralid (F)</b> LOAs (mg/kg) range from: to: <b>Toxicological reference values</b> ADI (mg/kg bw/day): 0.15 ARID (mg/kg bw): 0.17 Source of ADI: Source of ARID: Year of evaluation: Year of evaluation:		<b>Input values</b> Details - chronic risk assessment Supplementary results - chronic risk assessment Details - acute risk assessment/children Details - acute risk assessment/adults								
Comments:												
Normal mode												
Chronic risk assessment: JMPR methodology (IED/TMDI)												
		No of diets exceeding the ADI : ---										
	Calculated exposure (% of ADI)	MS Diet	Exposure (µg/kg bw per day)	Highest contributor to MS diet (in % of ADI)	Commodity / group of commodities	2nd contributor to MS diet (in % of ADI)	Commodity / group of commodities	3rd contributor to MS diet (in % of ADI)	Commodity / group of commodities	Exposure resulting from MRLs set at the LOO (in % of ADI)	commodities not under assessment (in % of ADI)	
TMDI(NED)/IEDI calculation (based on average food consumption)	4%	NL child	5.65	2%	Wheat	2%	Sugar beet roots	0.0%	Beetroots			
	4%	GEMS/Food G08	5.61	3%	Wheat	0.3%	Sugar beet roots	0.0%	Beetroots			
	3%	IT toddler	4.65	3%	Wheat		Grapefruits					
	3%	NL toddler	4.60	2%	Wheat	1%	Sugar beet roots	0.1%	Beetroots			
	3%	FR child 3-15 yr	4.45	2%	Wheat	0.8%	Sugar beet roots	0.0%	Beetroots			
	3%	RO general	3.58	2%	Wheat	0.3%	Sugar beet roots	0.0%	Beetroots			
	3%	UK toddler	3.78	2%	Wheat	0.7%	Sugar beet roots	0.0%	Beetroots			
	2%	GEMS/Food G15	3.34	2%	Wheat	0.1%	Beetroots	0.0%	Rapeseeds/canola seeds			
	2%	ES child	3.16	2%	Wheat	0.0%	Sugar beet roots	0.0%	Beetroots			
	2%	GEMS/Food G07	3.13	2%	Wheat	0.1%	Beetroots	0.0%	Rapeseeds/canola seeds			
	2%	DK child	3.10	2%	Wheat	0.0%	Beetroots	0.0%	Rapeseeds/canola seeds			
	2%	FR toddler 2-3 yr	3.09	1%	Wheat	0.6%	Sugar beet roots	0.0%	Beetroots			
	2%	DE women 14-50 yr	2.98	1%	Wheat	1.0%	Sugar beet roots	0.0%	Beetroots			
	2%	GEMS/Food G08	2.97	2%	Wheat	0.1%	Sugar beet roots	0.0%	Rapeseeds/canola seeds			
	2%	DE child	2.96	2%	Wheat	0.0%	Beetroots	0.0%	Rapeseeds/canola seeds			
	2%	GEMS/Food G10	2.91	2%	Wheat	0.1%	Beetroots	0.0%	Rapeseeds/canola seeds			
	2%	IT adult	2.90	2%	Wheat	0.0%	Beetroots					
	2%	GEMS/Food G11	2.84	2%	Wheat	0.2%	Grapefruits					
	2%	PT general	2.74	2%	Wheat		Grapefruits					
	2%	DE general	2.68	0.9%	Sugar beet roots	0.9%	Wheat	0.0%	Beetroots			
	2%	NL general	2.34	0.8%	Wheat	0.6%	Sugar beet roots	0.0%	Beetroots			
	2%	SE general	2.32	1%	Wheat	0.1%	Beetroots					
	2%	UK infant	2.29	1%	Wheat	0.3%	Sugar beet roots					
	1%	FR adult	1.84	1%	Wheat	0.2%	Sugar beet roots	0.0%	Beetroots			
	1%	IE adult	1.72	1%	Wheat	0.1%	Beetroots					
	1%	ES adult	1.69	1%	Wheat	0.0%	Sugar beet roots	0.0%	Beetroots			
	1%	UK vegetarian	1.62	1.0%	Wheat	0.1%	Sugar beet roots	0.0%	Beetroots			
	0.9%	UK adult	1.36	0.8%	Wheat	0.1%	Sugar beet roots	0.0%	Beetroots			
	0.7%	FR infant	0.98	0.4%	Wheat	0.3%	Sugar beet roots	0.0%	Beetroots			
	0.6%	FI 3 yr	0.93	0.6%	Wheat	0.1%	Beetroots					
	0.6%	LT adult	0.86	0.5%	Wheat	0.1%	Beetroots	0.0%	Rapeseeds/canola seeds			
	0.5%	IE child	0.82	0.5%	Wheat	0.0%	Beetroots					
	0.5%	FI 6 yr	0.79	0.5%	Wheat	0.1%	Beetroots					
	0.5%	DK adult	0.79	0.5%	Wheat		Grapefruits					
	0.2%	FI adult	0.28	0.1%	Wheat	0.0%	Beetroots	0.0%	Rapeseeds/canola seeds			
	0.1%	PL general	0.22	0.1%	Beetroots		Grapefruits					
	<b>Conclusion:</b> The estimated long-term dietary intake (TMDI(NED)/IEDI) was below the ADI. The long-term intake of residues of clopyralid (F) is unlikely to present a public health concern.											
	Acute risk assessment / children		Acute risk assessment / adults / general population				Acute risk assessment / children		Acute risk assessment / adults / general population			
	Details - acute risk assessment / children		Details - acute risk assessment / adults				Hide IESTI new calculations		Show IESTI new calculations			
	The acute risk assessment is based on the ARID. The calculation is based on the large portion of the most critical consumer group.						<b>ESTI new calculations:</b> The calculation is performed with the MRL and the peeling/processing factor (PF), taking into account the residue in the edible portion and/or the conversion factor for the residue definition (CF). For case 2a, 2b and 3 calculations a variability factor of 3 is used. Since this methodology is not based on internationally agreed principles, the results are considered as indicative only. Since this methodology is not based on internationally agreed principles, the results are considered as indicative only.					
Show results of IESTI calculation for all crops												
Unprocessed commodities	Results for children No. of commodities for which ARID/ADI is exceeded (ESTI):		Results for adults No. of commodities for which ARID/ADI is exceeded (ESTI):		Results for children No. of commodities for which ARID/ADI is exceeded (ESTI new):		Results for adults No. of commodities for which ARID/ADI is exceeded (ESTI new):					
	ESTI		ESTI		ESTI new		ESTI new					
	Highest % of ARID/ADI	Commodities	MRL / input for RA (mg/kg)	Exposure (µg/kg bw)	Highest % of ARID/ADI	Commodities	MRL / input for RA (mg/kg)	Exposure (µg/kg bw)				
	34%	Beetroots	1 / 1	57	14%	Beetroots	1 / 1	23	25%	Wheat	3 / 3	43
	6%	Wheat	3 / 0.7	10	3%	Wheat	3 / 0.7	5.9	14%	Beetroots	1 / 1	24
	0.02%	Rapeseeds/canola	0.5 / 0.03	0.03	0.01%	Rapeseeds/canola seeds	0.5 / 0.03	0.01	0.4%	Rapeseeds/canola	0.5 / 0.5	0.69
Expand/collapse list												
Total number of commodities exceeding the ARID/ADI in children and adult diets (ESTI calculation)						Total number of commodities found exceeding the ARID/ADI in children and adult diets (ESTI new calculation)						
Processed commodities	Results for children No. of processed commodities for which ARID/ADI is exceeded (ESTI):		Results for adults No. of processed commodities for which ARID/ADI is exceeded (ESTI):		Results for children No. of processed commodities for which ARID/ADI is exceeded (ESTI new):		Results for adults No. of processed commodities for which ARID/ADI is exceeded (ESTI new):					
	ESTI		ESTI		ESTI new		ESTI new					
	Highest % of ARID/ADI	Processed commodities	MRL / input for RA (mg/kg)	Exposure (µg/kg bw)	Highest % of ARID/ADI	Processed commodities	MRL / input for RA (mg/kg)	Exposure (µg/kg bw)				
	26%	Beetroots / boiled	1 / 1	44	23%	Beetroots / boiled	1 / 1	39	65%	Sugar beets (root) / sugar	1 / 12	110
	21%	Sugar beets (root) / sugar	1 / 3.84	35	8%	Sugar beets (root) / sugar	1 / 3.84	14	23%	Wheat / milling (flour)	3 / 3.21	39
	5%	Wheat / milling (flour)	3 / 0.75	9.1	2%	Wheat / pasta	3 / 0.75	2.9	11%	Beetroots / boiled	1 / 1	19
	2%	Wheat / milling (wholemeal)	3 / 0.52	2.9	1%	Wheat / bread	3 / 0.52	1.8	7%	Wheat / milling	3 / 2.22	12
	0.0%	Rapeseeds / oils	0.5 / 0.05	0.01	0.2%	Wheat / bread/pizza	3 / 0.06	0.28	0.2%	Rapeseeds / oils	0.5 / 1	0.29
		ILICZBA	ILICZBA	ILICZBA	ILICZBA	ILICZBA	ILICZBA	ILICZBA	ILICZBA	ILICZBA	ILICZBA	ILICZBA
		ILICZBA	ILICZBA	ILICZBA	ILICZBA	ILICZBA	ILICZBA	ILICZBA	ILICZBA	ILICZBA	ILICZBA	ILICZBA
Expand/collapse list												
<b>Conclusion:</b> No exceedance of the toxicological reference value was identified for any unprocessed commodity. A short term intake of residues of clopyralid (F) is unlikely to present a public health risk. For processed commodities, no exceedance of the ARID/ADI was identified.												

## New calculations results:



## **Combined exposure and risk assessment**

The product has one active substance.

### **7.2.1 Chronic consumer risk assessment from combined exposure**

The uses under consideration provide only a minor contribution to the overall chronic exposure of consumers to pesticide residues. The issue requires a more universal consideration and possibly the generic usage of monitoring data. A harmonised approach is not yet available, and currently no specific consideration is warranted in the scope of this evaluation.

### 7.3 References

- *EFSA Journal* 2018;16(7):5389
- : *Renewal Assessment Report Vol.3 B.7 – 2018;*

#### Summary of the evaluation

The preparation CHR/H/CPD 300 SL is composed of clopyralid.

**Table 7.3-1: Toxicological reference values for the dietary risk assessment of clopyralid**

Reference value	Source	Year	Value	Study relied upon	Safety factor
Clopyralid					
ADI	<i>EFSA Journal</i> 2018;16(7):5389	2018	0.15 mg/kg bw per day	rat, 2 year chronic toxicity and oncogenicity study	100
ARfD	<i>EFSA Journal</i> 2018;16(7):5389	2018	0.17 mg/kg bw	rabbit, developmental toxicity	300

#### Summary for clopyralid

**Table 7.3-2: Summary for clopyralid**

Use- No.*	Crop	Plant metabolism covered?	Sufficient residue trials?	PHI sufficiently supported?	Sample storage covered by stability data?	MRL compliance	Chronic risk for consumers identified?	Acute risk for consumers identified?
1, 2, 3, 4	Winter oilseed rape	Yes	Yes	-	Yes	Yes	No	No
5	Winter wheat	Yes	Yes	-	Yes	Yes	No	No
6, 7	Sugar beet	Yes	Yes	-	Yes	Yes	No	No

\* Use number(s) in accordance with the list of all intended GAPs in Part B, Section 0 should be given in column 1

#### Summary for CHR/H/CPD

**Table 7.3-3: Information on CHR/H/CPD 300 SL (KCA-6.8)**

Crop	PHI for CHR/H/CPD proposed by applicant	PHI/ Withholding period <sup>±</sup> sufficiently supported for	PHI for CHR/H/CPD 300SL proposed by zRMS	zRMS Comments (if different PHI proposed)
		clopyralid		
Winter oilseed rape(spring)	PHIs are not required. They are determined by the growth stages of crops at application.	NR		
Winter oilseed rape(autumn)		NR		
Winter wheat		NR		
Sugar beet		NR		

Crop	PHI for CHR/H/CPD proposed by applicant	PHI/ Withholding period* sufficiently supported for	PHI for CHR/H/CPD 300SL proposed by zRMS	zRMS Comments (if different PHI proposed)
		eoppyralid		
Sugar beet		NR		

NR: not relevant

\* Purpose of withholding period to be specified

\*\* F: PHI is defined by the application stage at last treatment (time elapsing between last treatment and harvest of the crop).

## Appendix 1 Lists of data considered in support of the evaluation

### 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
KCA 6.3/01	C. Lefebvre	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Sugar Beets Following One Foliar application with FAWORYT 300 SL under Field Conditions in Northern Europe in 2022.</i> ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2105 GLP YES Unpublished	N	PUH Chemirol
KCA 6.3/02	C. Lefebvre	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Sugar Beets Following One Foliar application with FAWORYT 300 SL under Field Conditions in Northern Europe in 2022.</i> ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2127 GLP YES Unpublished	N	PUH Chemirol
KCA 6.3/03	C. Lefebvre	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Sugar Beets Following One Foliar application with FAWORYT 300 SL under Field Conditions in Northern Europe in 2022.</i> ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2128 GLP YES Unpublished	N	PUH Chemirol
KCA 6.3/04	C. Lefebvre	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Sugar Beets Following One Foliar application with FAWORYT 300 SL under Field Conditions in Northern Europe in 2022.</i> ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2129 GLP YES Unpublished	N	PUH Chemirol
KCA 6.3/05	C. Lefebvre	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Sugar Beets Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022.</i> ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2130 GLP YES Unpublished	N	PUH Chemirol
KCA 6.3/06	C. Lefebvre	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Sugar Beets Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022.</i> ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2131 GLP YES Unpublished	N	PUH Chemirol
KCA 6.3/07	C. Lefebvre	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Sugar Beets Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022.</i> ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2132 GLP YES Unpublished	N	PUH Chemirol
KCA 6.3/08	C. Lefebvre	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Sugar Beets Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022.</i> ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2133	N	PUH Chemirol



<b>Data point</b>	<b>Author(s)</b>	<b>Year</b>	<b>Title Company Report No. Source (where different from company) GLP or GEP status Published or not</b>	<b>Vertebrate study Y/N</b>	<b>Owner</b>
			GLP YES Unpublished		
KCA 6.3/09	C. Lefebvre	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Sugar Beets Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022.</i> ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2134 GLP YES Unpublished	N	PUH Chemirol
KCA 6.3/10	E. Thomas-Delille	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Oilseed Rape Following One Foliar application with FAWORYT 300 SL under Field Conditions in Northern Europe in 2022.</i> ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2104 GLP YES Unpublished	N	PUH Chemirol
KCA 6.3/11	E. Thomas-Delille	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Oilseed Rape Following One Foliar application with FAWORYT 300 SL under Field Conditions in Northern Europe in 2022.</i> ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2120 GLP YES Unpublished	N	PUH Chemirol
KCA 6.3/12	E. Thomas-Delille	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Oilseed Rape Following One Foliar application with FAWORYT 300 SL under Field Conditions in Northern Europe in 2022.</i> ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2121 GLP YES Unpublished	N	PUH Chemirol
KCA 6.3/13	E. Thomas-Delille	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Oilseed Rape Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022.</i> ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2122 GLP YES Unpublished	N	PUH Chemirol
KCA 6.3/14	E. Thomas-Delille	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Oilseed Rape Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022.</i> ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2123 GLP YES Unpublished	N	PUH Chemirol
KCA 6.3/15	E. Thomas-Delille	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Oilseed Rape Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022.</i> ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2124 GLP YES Unpublished	N	PUH Chemirol
KCA 6.3/16	E. Thomas-Delille	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Oilseed Rape Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022.</i> ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2125 GLP YES	N	PUH Chemirol

<b>Data point</b>	<b>Author(s)</b>	<b>Year</b>	<b>Title Company Report No. Source (where different from company) GLP or GEP status Published or not</b>	<b>Vertebrate study Y/N</b>	<b>Owner</b>
			<i>Unpublished</i>		
KCA 6.3/17	E. Thomas-Delille	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Oilseed Rape Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022. ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2126 GLP YES Unpublished</i>	N	PUH Chemirol
KCA 6.3/18	E. Schneider	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Winter Wheat Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022 ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2114 GLP YES Unpublished</i>	N	PUH Chemirol
KCA 6.3/19	E. Schneider	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Winter Wheat Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022 ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2115 GLP YES Unpublished</i>	N	PUH Chemirol
KCA 6.3/20	E. Schneider	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Winter Wheat Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022 ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2116 GLP YES Unpublished</i>	N	PUH Chemirol
KCA 6.3/21	E. Schneider	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Winter Wheat Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022 ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2117 GLP YES Unpublished</i>	N	PUH Chemirol
KCA 6.3/22	E. Schneider	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Winter Wheat Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022 ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2103 GLP YES Unpublished</i>	N	PUH Chemirol
KCA 6.3/23	E. Schneider	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Winter Wheat Following One Foliar application with FAWORYT 300 SL under Field Conditions in Northern Europe in 2022 ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2111 GLP YES Unpublished</i>	N	PUH Chemirol
KCA 6.3/24	E. Schneider	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Winter Wheat Following One Foliar application with FAWORYT 300 SL under Field Conditions in Northern Europe in 2022 ANADIAG, 16, rue Ampère, 67500 HAGUENAU, France Study No. C2112 GLP YES Unpublished</i>	N	PUH Chemirol

<b>Data point</b>	<b>Author(s)</b>	<b>Year</b>	<b>Title</b> <b>Company Report No.</b> <b>Source (where different from company)</b> <b>GLP or GEP status</b> <b>Published or not</b>	<b>Vertebrate study Y/N</b>	<b>Owner</b>
KCA 6.3/25	E. Schneider	2023	<i>Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Winter Wheat Following One Foliar application with FAWORYT 300 SL under Field Conditions in Northern Europe in 2022</i> Study No. C2118 GLP YES Unpublished	N	PUH Chemirol

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

<b>Data point</b>	<b>Author(s)</b>	<b>Year</b>	<b>Title</b> <b>Company Report No.</b> <b>Source (where different from company)</b> <b>GLP or GEP status</b> <b>Published or not</b>	<b>Vertebrate study Y/N</b>	<b>Owner</b>
KCA 6.1	Dial, E., Lindsay, D.	2006	<i>Frozen Storage Stability of Clopyralid in Oilseed Rape</i> DAS Study No. 020122.02 CEM Analytical Services (CEMAS), North Ascot, Berkshire, UK GLP/GEP (Y/N): Yes Published (Y/N): No	N	DAS
KCA 6.1	Foster, D.R., Blakeslee, B.A., Rutherford, B.S.	1996	<i>Frozen Storage Stability of Clopyralid, 2,4-D in Corn Grain, Straw and Fodder</i> DAS Study No. RES93050.01 Dow Elanco, Indianapolis, Indiana, US GLP/GEP (Y/N): Yes Published (Y/N): No	N	DAS
KCA 6.1	Clements, B, Bolton, A	1996	<i>Determination of the Stability of Clopyralid Residues in Pasture under Frozen Storage Conditions</i> DAS Study No. GHE-P-5350 CEM Analytical Services (CEMAS), North Ascot, Berkshire, UK GLP/GEP (Y/N): Yes Published (Y/N): No	N	DAS
KCA 6.1		2004	<i>Frozen Storage Stability of Clopyralid in Beef Muscle, Liver, Kidney, Milk and Chicken Egg</i> Study No. 020120.01 GLP/GEP (Y/N): Yes Published (Y/N): No LoA	N	DAS
KCA 6.1		2015	<i>Frozen Storage Stability of Clopyralid in Bovine Fat</i> Study No. 120602 GLP/GEP (Y/N): Yes Published (Y/N): No LoA	N	DAS
KCA 6.2.1	Chapleo So. Caley C.Y.	2002	The metabolism of [14C]-Clopyralid in Sugar Beet DAS Study No. GHE-P-9939 Inveresk Research International, Tranent, East Lothian, United Kingdom GLP: Y Unpublished	N	DAS

KCA 6.2.1	Guo C.	1996	Metabolism of 14C-Clopyralid in Cabbage DAS Study No. GH-C-4289 ABC Laboratories Inc., Columbia, Missouri, USA GLP: Y Unpublished	N	DAS
KCA 6.2.1	Chapleo So. Caley C.Y.	2002	The metabolism of (14C)-Clopyralid in Oilseed Rape DAS Study No. GHE-P-9938 Inveresk Research International, Tranent, East Lothian, United Kingdom GLP: Y Unpublished	N	DAS
KCA 6.2.2- 6.2.5		2015	A Nature of the Residue Study in the Ruminant with [14C]Clopyralid Study No. 130202 GLP/GEP (Y/N): Yes Published (Y/N): No LoA	N	DAS
KCA 6.2.2- 6.2.5		2014	A Nature of the Residue Study in the Laying Hen with [14C]-Clopyralid Study No. 130906 GLP/GEP (Y/N): Yes Published (Y/N): No Dow AgroSciences LLC, Indianapolis, Indiana, USA LoA	Y	DAS
KCA 6.4.1- 6.4.3		1974	Dowco 290 and 2,4-D Chicken Feeding Study DAS Study No. TA-517 GLP: Y Unpublished	Y	DAS
KCA 6.4.1- 6.4.3		1975	Residues of Dowco 290 (3,6-dichloropicolinic acid) in Tissues of Chicken Fed the Herbicide DAS Study No. GH-C 819 GLP: N Unpublished	Y	DAS
KCA 6.4.1- 6.4.3		2015	Summary of Clopyralid Livestock Feeding Study: Magnitude of Residue in Eggs, Muscle, Liver and Fat of Laying Hens DAS Study No. 150031 Lab Study No. CEMS-6921 GLP: Y Unpublished	Y	DAS
KCA 6.4.1- 6.4.3		1974	Milk Residue Study with Dairy Cows Fed Lontrel Herbicide, Nellite Nematocide and 2,4-D Herbicide: Animal Care, Sampling and Production Records DAS Study No. GH-A 579 GLP: N Unpublished	Y	DAS
KCA 6.4.1- 6.4.3		1974	Residues of Dowco 290 (3,6-dichloropicolinic acid) in Milk and Cream from Cows Fed the Herbicide DAS Study No. GH-C 745 GLP: N Unpublished	Y	DAS

KCA 6.4.1- 6.4.3		1975	Residues of Dowco 290 (3,6-dichloropicolonic acid) in Bovine Tissues from Calves Fed the Herbicide DAS Study No. GH-C 811 GLP: N Unpublished	Y	DAS
KCA 6.4.1- 6.4.3		2015	Summary of Clopyralid Livestock Feeding Study: Magnitude of Residue in Milk, Muscle, Liver and Fat of Lactating Dairy Cattle DAS Study No. 150030 Lab Study No. CEMS-6968 GLP: Y Unpublished	Y	DAS
KCA 6.5.1	Adusumili H.	2014	Processing Study to Determine the Nature of Residues of 14C -Clopyralid Following the Industrial or Household Preparation DAS Study No. 140574 Dow AgroSciences LLC, Indianapolis, Indiana, USA GLP/GEP (Y/N): Yes Published (Y/N): No	N	DAS
KCA 6.5.1	Devine, H.C.	2006	Residues of clopyralid in wheat and process fractions at harvest following a single application of EF-1498, Northern France - 2005 DAS Study No. GHE-P-11274 CEM Analytical Services - UK GLP/GEP (Y/N): Yes Published (Y/N): No	N	DAS
KCA 6.6.1	Hall, L. R.	2015	14C -Clopyralid: Metabolism in Confined Rotational Crops with a 30-Day Plant-back Interval DAS Study No. 130733 ABC Laboratories, Inc., Columbia, Missouri 65202, USA GLP/GEP (Y/N): Yes Published (Y/N): No	N	DAS
KCA 6.6.1	Yackovich P.R., Lardie T.S. Brink D.L.	1993	A 10-1/2 Month Rotational Crops Study With 14C-Labeled Clopyralid – MET90080 DAS Study Np. GH-C-2992 Dow AgroSciences LLC, Indianapolis, Indiana, United States GLP: Y Unpublished	N	DAS
KCA 6.6.1	Yackovich P.R., Lardie T.S. Miller J.H.	1989	A 125-Day Rotational Crops Study With 14C-Labelled Clopyralid DAS Study Np. GH-C-2277 DowElanco, Midland, Michigan, USA GLP: Y Unpublished	N	DAS
KCA 6.3	Jones, EM Yuill, MM	1976a	Determination of Residues of 3,6-dichloropicolonic Acid (DOWCO 290) in Rape Seed Oil and Cake from 1975 Trials Carried Out by the Boots Company Limited Dow Chemical Company DAS Report No.: GHE-P-325 GLP:N Unpublished	N	DAS

KCA 6.3	Jones, EM Yuill, MM	1976b	Determination of Residues of 3,6-dichloropicolinic Acid (DOWCO 290) in Rape Seed, Cake, Oil and Straw from a Trial Carried Out in 1975 in Sweden by BT KEMI Dow Chemical Company DAS Report No.: GHE-P-337 GLP:N Unpublished	N	DAS
KCA 6.3	Rawle N.W. Khoshab A.	2002	Residues of Clopyralid in Oilseed Rape at Intervals and at Harvest Following Multiple Applications of Lontrel 100 (EF-1136), EU Northern Zone – 2001. DAS Report No.: GHE-P-9380 GLP: Y Unpublished	N	DAS
KCA 6.3	Freeman JMH Walker SM	1980	Determination of Residues of 3,6-dichloropicolinic Acid (DOWCO* 290) in Sugar Beet, Roots and Tops, Treated with FORMAT** - UK 1980 Dow Chemical Company DAS Report No.: GHE-P-803 GLP:N Unpublished	N	DAS
KCA 6.3	Rawle N.W. Khoshab A.	2002	Residues of Clopyralid in Sugarbeet at Intervals Under Open Field Conditions Following Multiple Applications of Lontrel 100 (EF-1136), Northern France and UK – 2000. DAS Report No.: GHE-P-9356 GLP: Y Unpublished	N	DAS
KCA 6.3	Rawle N.W. Khoshab A.	2002	Residues of Clopyralid in Sugar Beet at Harvest Under Open Field Conditions Following Multiple Applications of Lontrel 100 (EF-1136), Northern France and UK – 2000. DAS Report No.: GHE-P-9357 GLP: Y Unpublished	N	DAS
KCA 6.3	Rawle N.W. Khoshab A.	2002	Residues of Clopyralid in Sugar Beet at Intervals and at Harvest Following Multiple Applications of Lontrel (EF-1136), Northern Zone – 2001. DAS Report No.: GHE-P-9381 GLP: Y Unpublished	N	DAS
KCA 6.3	Freeman, JMH at al	1982	Effect of Length of Period Between Application of CYRONAL* and Harvest on Residues of 3,6-dichloropicolinic Acid (DOWCO 290**) in Winter Wheat, Winter Barley and Maize – Belgium 1981 Dow Chemical Company DAS Report No.: GHE-P-943 GLP:N Unpublished	N	DAS
KCA 6.3	Freeman, JMH	1984	Clopyralid Residues in Wheat Grain and Straw Treated with Either LONPAR* or LONTREL* 100 from French Trials, 1983 Dow Chemical Company DAS Report No.: GHE-P-1258 GLP:N Unpublished	N	DAS

KCA 6.3	Rawle N.W. Khoshab A.	2002	Residues of Clopyralid in Wheat at Intervals Under Open Field Conditions Following a Single Application of Lontrel (EF-1136), UK and Germany – 2000. DAS Report No.: GHE-P-9358 GLP:Y Unpublished	N	DAS
KCA 6.3	Rawle N.W. Khoshab A.	2002	Residues of Clopyralid in Wheat at Intervals Under Open Field Conditions Following a Single Application of Lontrel 100 (EF-1136), EU Northern Zone – 2001. DAS Report No.: GHE-P-9385 GLP:Y Unpublished	N	DAS
KCA 6.3	Freeman, JMH	1982	Effect of Length of Period Between Application of CYRONAL* and Harvest on Residues of 3,6-dichloropicolinic Acid (DOWCO 290**) in Winter Wheat, Winter Barley and Maize – Belgium 1981 Dow Chemical Company DAS Report No.: GHE-P-943 GLP:N Unpublished	N	DAS
KCA 6.3	Rawle N.W. Khoshab A.	2002	Residues of Clopyralid in Barley at Intervals and at Harvest Following a Single Application of Lontrel 100 (EF-1136), EU Northern Zone – 2001. DAS Report No.: GHE-P-9383 GLP:Y Unpublished	N	DAS
KCA 6.3	Rawle N.W. Khoshab A.	2002	Residues of Clopyralid in Barley at Intervals Under Open Field Conditions Following a Single Application of Lontrel (EF-1136), UK – 2000. DAS Report No.: GHE-P-9360 GLP:Y Unpublished	N	DAS
KCA 6.3	Rawle N.W. Khoshab A.	2002	Residues of Clopyralid in Barley at Harvest in Open Field Conditions Following a Single Application of Lontrel 100 (EF-1136), UK – 2000. DAS Report No.: GHE-P-9359 GLP:Y Unpublished	N	DAS

**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 and 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
-	-	-	-	-	-





## **Appendix 2 Detailed evaluation of the additional studies relied upon**

### **A 2.1.1 Stability of residues**

#### **A 2.1.1.1 Stability of residues during storage of samples**

##### **A 2.1.1.1.1 Storage stability of residues in plant products**

No new studies submitted.

##### **A 2.1.1.1.2 Storage stability of residues in animal products**

No new studies submitted.

### **A 2.1.2 Nature of residues in plants, livestock and processed commodities**

#### **A 2.1.2.1 Nature of residue in plants**

No new studies submitted.

##### **A 2.1.2.1.1 Nature of residue in rotational crops**

Data matching studies have been evaluated by RMS - Finland. As a result of the assessment all reports were accepted and considered as equivalent to protected studies. Therefore, to support the renewal of authorization of CHR/H/CPD300SL/Major 300SL, Cloe 300SL, ProSto 300SL INNVIGO is allowed to refer to EU approved reports.

##### **A 2.1.2.1.2 Nature of residues in processed commodities**

###### **A 2.1.2.1.3.1 Study 1**

Data matching studies have been evaluated by RMS - Finland. As a result of the assessment all reports were accepted and considered as equivalent to protected studies. Therefore, to support the renewal of authorization of CHR/H/CPD300SL/Major 300SL, Cloe 300SL, ProSto 300SL INNVIGO is allowed to refer to EU approved reports.

#### **A 2.1.2.2 Nature of residues in livestock**

Data matching studies have been evaluated by RMS - Finland. As a result of the assessment all reports were accepted and considered as equivalent to protected studies. Therefore, to support the renewal of authorization of CHR/H/CPD300SL/Major 300SL, Cloe 300SL, ProSto 300SL INNVIGO is allowed to refer to EU approved reports.

### **A 2.1.3 Magnitude of residues in livestock**

No new studies submitted.

#### **A 2.1.3.1 Livestock feeding studies**

Data matching studies have been evaluated by RMS - Finland. As a result of the assessment all reports were accepted and considered as equivalent to protected studies. Therefore, to support the renewal of authorization of CHR/H/CPD300SL/Major 300SL, Cloe 300SL, ProSto 300SL INNVIGO is allowed to refer to EU approved reports.

## Sugar beet

**March 2024**

The applicant provided the new residue trials.

The objective of the studies were to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Sugar beet raw agricultural commodity (RAC) after one foliar application (at BBCH 14) of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.5 L/ha. Nine independent trials (North France, Germany, Hungary, Czech Republic and Poland) are accepted and valid in relation to storage stability data. Residues are below MRL established for sugar beet roots (Reg. (EU) 2021/1807).

Note: The maps presented in the studies do not contain the correct locations of the studies.

### A 2.1.3a A 2.1.3 Magnitude of residues in plants

#### A 2.1.3.1.1.1 Study 1

Reference:	KCA 6.3/01
Report	Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Sugar Beets Following One Foliar application with FAWORYT 300 SL under Field Conditions in Northern Europe in 2022, M. Lefebvre 2023, C2105, Anadiag, France
Guideline(s):	Regulation (EC) No. 1107/2009 Regulation (EU) No. 283/2013 and 284/2013 2004/10/EC GLP Directive OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021 SANTE/2019/12752 - Technical guidelines on data requirements for setting Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin. SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.
Deviations:	No
GLP:	Yes
Acceptability:	Yes

#### Objective of the study

The objective of the study was to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Sugar beet raw agricultural commodity (RAC) after one foliar application of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.5 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at 1 site in Northern Europe. The trial was sampled frequently to monitor the decline of residues shortly after the treatment.

One plot was treated once with FAWORYT 300 SL at BBCH 14, at the application rate of 0.5 L/ha (150 g clopyralid/ha).

One plot remained untreated.

Sampling was performed at 0 DBA (Day before Application) in untreated plot, 0 DAA (Day after application) in treated plot, 7 DAA; 20 DAA, 40 DAA in treated plot. Final sampling was performed at normal commercial harvest (BBCH 49) in treated and untreated plots.

Clopyralid (Sum of clopyralid, its salts and conjugates) residues were analysed in samples harvested during the field phase.

### Field phase description

The objective of the study was to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Sugar beet raw agricultural commodity (RAC) after one foliar application of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.5 L/ha.

The following pattern was designed for the treatments and the samplings:

#### 1.1.1.1 Application details

Plot	Test Item	App. No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	<b>FAWORYT 300 SL</b>	T1	BBCH 14	0.5 L/ha	150 g/ha	200-300 L/ha (±10%)



#### 1.1.1.2 Sampling Details

##### Decline curve trial

Sampling event	Plot	Timing	Matrix	Min. Sample size
S1	U	0 DBA	Whole plants	0.1 kg and min. 12 plants
	T	0 DAA	Whole plants	0.1 kg and min. 12 plants
S2	T	7 (±1) DAA	Whole plants	0.1 kg and min. 12 plants
S3	T	21 (±2) DAA	Whole plants	0.1 kg and min. 12 plants
S4	T	40 (±2) DAA	Roots	0.5 kg, from min. 12 plants
			Leaves with tops	0.5 kg, from min. 12 plants
S5	U, T	NCH BBCH 49	Roots	2 kg, from min. 12 plants
			Leaves with tops	1 kg, from min. 12 plants

DBA : Days before application

DAA : Days after application

NCH: Normal Commercial harvest

##### Location of the trial

The trial was performed on soil type and under cultural practices typical for sugar beet production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Type of trial	Crop	European area	Region, Country
1	C2105 AN1	Maxime SCHMITT	DC	Sugar beet	North	Grand Est, France

DC: Decline curve

##### Identity and composition of the test item(s):

###### Test item

Trade or Code Name	FAWORYT 300 SL
Active substance (a.s.)	Clopyralid (as clopyralid monoethanolamine salt)
Formulation type	SL
CAS Number	[1702-17-6] ([57754-85-5])
Nominal content of a.s.	300 g/L (expressed as clopyralid)
Batch number*	202203001
Actual content *	302.2 g/L (expressed as clopyralid)
Expiry date*	11/03/2025

##### General Information on the trial

###### Crop and soil Information

Trial No.	Crop	Variety	Crop density (plants/ha)	Sowing / Planting date	Soil type	pH	Organic matter (%)
C2105 AN1	Sugar beet	Jellera KWS	≈ 111 111	24/03/2022	Silty clay	6.8	2.2

##### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (m)	Pressure (bars)
C2105 AN1	AGRISER	Flat fan	Teejet XR 110 015 VS	3.0	9	0.33	2.2

##### Summary of the actual application(s) data

Trial No.	Plot	Application No.	Active substance rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2105 AN1	T	1	157.5	+5.0	210	12/05/2022	14

## Sampling of specimens

### Sampling summary

Trial No	Sampling	Actual Date	Actual timing	Actual Growth Stage (BBCH)
C2105 AN1	1	12/05/2022	0 DBA / 0 DAA	14
	2	19/05/2022	7 DAA	18
	3	01/06/2022	20 DAA	19-31
	4	21/06/2022	40 DAA	39
	5	21/09/2022	132 DAA, NCH	49

DAA: Days after application

DBA: Day before application

NCH: Normal commercial harvest

## ANALYTICAL PHASE

The objective of the analytical phase was to determine the residue levels of clopyralid in samples harvested during the field phase.

### Experimental details

#### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trial.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

### Storage stability of specimens

Specimens were stored frozen for no more than 271 days from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in commodities with high water, high oil, high acid and dry/high starch content (EFSA Journal Volume19, Issue1, January 2021, e06389).

### Storage stability of extracts

After extraction, samples were stored refrigerated and analysed after maximum 9 days.

Results of storage stability of extracts in ANADIAG validation study No. C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities” showed a good stability of clopyralid residues for up to 15 days of refrigerated storage for high water content.

### Specimen preparation

The specimens were prepared according to ANADIAG SOPs.

The sample was blended with dry ice and placed for at least 12 hours at  $T < -18^{\circ}\text{C}$  for sublimation of dry ice. The amount required by the analytical method (2 g) was weighed from this homogeneous matrix.

### Specimen analysis

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

#### Outline of ANADIAG method:

Residues of clopyralid and its conjugates are extracted and hydrolysed from samples by heating at 60 °C for 3 hours with 2.5M KOH. After acidification with H<sub>2</sub>SO<sub>4</sub>, addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract is purified with a liquid-liquid partition. An aliquot of the upper layer is evaporated to dryness and the sample is reconstituted in 50:50, methanol/H<sub>2</sub>O + 0.1% formic acid. Extracts are analysed by LC-MS/MS.

ANADIAG References (French version) of the method are  
for the preparation and extraction of the samples: SOP MP 718  
for the analysis of extracts and for the calibration: SOP MA 1809

#### LOD

The limit of detection (LOD) was expressed as lowest calibration standard.

The LOD was 0.4 ng/mL for clopyralid in high water content (corresponding to 0.002 mg/kg for clopyralid and 0.003 mg/kg for clopyralid glycine).

#### LOQ

The LOQ was 0.01 mg/kg for clopyralid and clopyralid glycine in high water content.

#### Preparation of standard solutions

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

	Solvent	Concentration	Storage conditions	Expiry date (Preparation + ...)
Stock solution Clopyralid	Acetonitrile	≈ 1 mg/mL	Frozen	6 months
Stock solution Clopyralid glycine	Methanol	≈ 1 mg/mL	Frozen	6 months
Spiking solutions All analyte separately	Acetonitrile	≈ 0.2, 2 and 20 µg/mL	Frozen	1 month
Intermediate calibration solutions Clopyralid <sup>(1)</sup>	Control extract	≈ 200 and 20 ng/mL	Refrigerated	14 days
Matrix-matched Calibration solutions Clopyralid <sup>(1)</sup>	Control extract	≈ 0.4 to 24 ng/mL	Refrigerated	14 days
Intermediate calibration solutions Clopyralid <sup>(2)</sup>	Methanol / water (50/50) + 0.1% formic acid	≈ 200 and 20 ng/mL	Refrigerated	14 days
Calibration solution Clopyralid <sup>(2)</sup>	Methanol / water (50/50) + 0.1% formic acid	≈ 0.4 to 24 ng/mL	Refrigerated	14 days

<sup>(1)</sup> For analysis of undiluted extracts

<sup>(2)</sup> For analysis of diluted extracts (dilution factor ≥ 20)

#### Calibration curves

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas of clopyralid obtained from chromatograms were plotted versus concentration and the calibration functions were determined by least square fit.

Number and concentrations of standards used, as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve (r) should be ≥ 0.990 for the calibration to be acceptable with regression residuals randomly distributed.

All extracts analysed (after dilution when required) fell within the range of the standard curve.

#### Fortification procedure

Fortifications were performed by adding known amounts of the spiking solutions to control specimens

just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

The spiked samples for roots and leaves with tops were done on untreated samples available at ANADIAG laboratory (ANADIAG sample No. S593 for whole plants, S595 for roots and S594 for leaves with tops). The absence of the analyte in these samples was checked within this study. The amount found was not detectable

(i.e. below the limit of detection, see detailed data in Appendix V).

Analytical Sample No.	Matrix	Fortification level (mg/kg)	Clopyralid % Recovery	Clopyralid glycine % Recovery	Extraction date
S593 01 AA	Whole plants	0.01	81.3%	-	07/02/2023
S593 01 BA	Whole plants	0.10	98.1%	-	08/02/2023
S593 01 CA	Whole plants	0.01	-	71.3%	08/02/2023
S593 01 DA	Whole plants	0.10	-	77.8%	07/02/2023
S593 01 EA d250	Whole plants	25	107.2%	-	15/02/2023
S593 01 FA d250	Whole plants	25	-	100.7%	15/02/2023
S594 01 AA	Leaves with tops	0.01	92.8%	-	09/02/2023
S594 01 BA	Leaves with tops	0.10	91.9%	-	10/02/2023
S594 01 CA	Leaves with tops	0.01	-	71.9%	10/02/2023
S594 01 DA	Leaves with tops	0.10	-	74.2%	09/02/2023
S594 01 EA d10	Leaves with tops	1.0	96.5%	-	15/02/2023
S594 01 FA d10	Leaves with tops	1.0	-	83.9%	15/02/2023
S595 01 AA	Roots	0.01	99.8%	-	13/02/2023
S595 01 BA	Roots	0.10	95.7%	-	14/02/2023
S595 01 CA	Roots	0.01	-	72.4%	14/02/2023
S595 01 DA	Roots	0.10	-	79.7%	13/02/2023
S595 01 EA D10	Roots	1.0	102.1%	-	17/02/2023
S595 01 FA D10	Roots	1.0	-	76.1%	17/02/2023

The recoveries of the spiked samples met with the acceptance criteria described in SANTE/2020/12830, Rev.1.

## Results

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2105 AN1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2105 01 01	C2105 AN1 / U1 / A	-	Whole plants	-	NDR
C2105 01 02	C2105 AN1 / T1 / A	FAWORYT 300 SL	Whole plants	0	13.54
C2105 01 03	C2105 AN1 / T2 / A	FAWORYT 300 SL	Whole plants	7	0.67
C2105 01 04	C2105 AN1 / T3 / A	FAWORYT 300 SL	Whole plants	20	0.43
C2105 01 05	C2105 AN1 / T4R / A	FAWORYT 300 SL	Roots	40	0.27
C2105 01 06	C2105 AN1 / T4L / A	FAWORYT 300 SL	Leaves with tops	40	0.36
C2105 01 07	C2105 AN1 / UHR / A	-	Roots	-	NDR
C2105 01 08	C2105 AN1 / UHL / A	-	Leaves with tops	-	NDR
C2105 01 09	C2105 AN1 / THR / A	FAWORYT 300 SL	Roots	132	0.04
C2105 01 10	C2105 AN1 / THL / A	FAWORYT 300 SL	Leaves with tops	132	0.08

DAA: Days After Application

NDR: No detectable residues (residues below the limit of detection)

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg



#### A 2.1.3.1.1.2 Study 2

Reference:	KCA 6.3/02
Report	Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Sugar Beets Following One Foliar application with FAWORYT 300 SL under Field Conditions in Northern Europe in 2022, M. Lefebvre 2023, C2127, Anadiag, France
Guideline(s):	Regulation (EC) No. 1107/2009 Regulation (EU) No. 283/2013 and 284/2013 2004/10/EC GLP Directive OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021 SANTE/2019/12752 - Technical guidelines on data requirements for setting Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin. SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.
Deviations:	No
GLP:	Yes
Acceptability:	Yes

#### Objective of the study

The objective of the study was to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Sugar beet raw agricultural commodity (RAC) after one foliar application of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.5 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at 1 site in Northern Europe. The trial was sampled frequently to monitor the decline of residues shortly after the treatment.

One plot was treated once with FAWORYT 300 SL at BBCH 14, at the application rate of 0.5 L/ha (150 g clopyralid/ha).

One plot remained untreated.

Sampling was performed at 0 DBA (Day before Application) in untreated plot, 0 DAA (Day after application) in treated plot, 7 DAA; 23 DAA, 42 DAA in treated plot. Final sampling was performed at normal commercial harvest (BBCH 49) in treated and untreated plots.

Clopyralid (Sum of clopyralid, its salts and conjugates) residues were analysed in samples harvested during the field phase.

#### Field phase description

The objective of the study was to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Sugar beet raw agricultural commodity (RAC) after one foliar application of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.5 L/ha.

The following pattern was designed for the treatments and the samplings:



#### 1.1.1.1 Application details

Plot	Test Item	App. No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	<b>FAWORYT 300 SL</b>	T1	BBCH 14	0.5 L/ha	150 g/ha	200-300 L/ha (±10%)

#### 1.1.1.2 Sampling Details

##### Decline curve trial

Sampling event	Plot	Timing	Matrix	Min. Sample size
<b>S1</b>	U	0 DBA	Whole plants	0.1 kg and min. 12 plants
	T	0 DAA	Whole plants	0.1 kg and min. 12 plants
<b>S2</b>	T	7 (±1) DAA	Whole plants	0.1 kg and min. 12 plants
<b>S3</b>	T	21 (±2) DAA	Whole plants	0.1 kg and min. 12 plants
<b>S4</b>	T	40 (±2) DAA	Roots	0.5 kg, from min. 12 plants
			Leaves with tops	0.5 kg, from min. 12 plants
<b>S5</b>	U, T	NCH BBCH 49	Roots	2 kg, from min. 12 plants
			Leaves with tops	1 kg, from min. 12 plants

DBA : Days before application

DAA : Days after application

NCH: Normal Commercial harvest

#### Location of the trial

The trial was performed on soil type and under cultural practices typical for sugar beet production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Type of trial	Crop	European area	Region, Country
1	<b>C2127 AN1</b>	Maxime SCHMITT	DC	Sugar beet	North	Grand Est, France

DC: Decline curve



#### Identity and composition of the test item(s):

##### Test item

<b>Trade or Code Name</b>	<b>FAWORYT 300 SL</b>
<b>Active substance (a.s.)</b>	Clopyralid (as clopyralid monoethanolamine salt)
<b>Formulation type</b>	SL
<b>CAS Number</b>	[1702-17-6] ([57754-85-5])
<b>Nominal content of a.s.</b>	300 g/L (expressed as clopyralid)
<b>Batch number*</b>	202203001
<b>Actual content *</b>	302.2 g/L (expressed as clopyralid)
<b>Expiry date*</b>	11/03/2025

#### General Information on the trial

##### Crop and soil Information

Trial No.	Crop	Variety	Crop density (plants/ha)	Sowing / Planting date	Soil type	pH	Organic matter (%)
C2127 AN1	Sugar beet	Rainette	≈ 111 110	23/03/2022	Silty clay	7.1	2.3

#### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (m)	Pressure (bars)
C2127 AN1	AGRISER	Flat fan	Teejet XR 110 015 VS	3.0	9	0.33	2.2

#### Summary of the actual application(s) data

Trial No.	Plot	Application No.	Active substance rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2127 AN1	T	1	161.0	+7.3	215	04/05/2022	14

#### Sampling of specimens

### Sampling summary

Trial No	Sampling	Actual Date	Actual timing	Actual Growth Stage (BBCH)
C2127 AN1	1	04/05/2022	0 DBA / 0 DAA	14
	2	11/05/2022	7 DAA	16
	3	27/05/2022	23 DAA	19
	4	15/06/2022	42 DAA	39
	5	13/09/2022	132 DAA, NCH	49

DAA: Days after application

DBA: Day before application

NCH: Normal commercial harvest

### ANALYTICAL PHASE

The objective of the analytical phase was to determine the residue levels of clopyralid in samples harvested during the field phase.

#### Experimental details

##### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trial.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

#### TRIAL No. C2127 AN1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2127 01 01	C2127 AN1 / U1 / A	04/05/2022	07/02/2023	279	11/02/2023	4
C2127 01 02	C2127 AN1 / T1 / A	04/05/2022	07/02/2023	279	16/02/2023	9
C2127 01 03	C2127 AN1 / T2 / A	11/05/2022	07/02/2023	272	16/02/2023	9
C2127 01 04	C2127 AN1 / T3 / A	27/05/2022	07/02/2023	256	11/02/2023	4
C2127 01 05	C2127 AN1 / T4R / A	15/06/2022	13/02/2023	243	18/02/2023	5
C2127 01 06	C2127 AN1 / T4L / A	15/06/2022	09/02/2023	239	16/02/2023	7
C2127 01 07	C2127 AN1 / UHR / A	13/09/2022	13/02/2023	153	17/02/2023	4
C2127 01 08	C2127 AN1 / UHL / A	13/09/2022	09/02/2023	149	11/02/2023	2
C2127 01 09	C2127 AN1 / THR / A	13/09/2022	13/02/2023	153	18/02/2023	5
C2127 01 10	C2127 AN1 / THL / A	13/09/2022	09/02/2023	149	16/02/2023	7

#### Storage stability of specimens

Specimens were stored frozen for no more than 279 days from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in commodities with high water, high oil, high acid and dry/high starch content (EFSA Journal Volume19, Issue1, January 2021, e06389).

#### Storage stability of extracts

After extraction, samples were stored refrigerated and analysed after maximum 9 days.

Results of storage stability of extracts in ANADIAG validation study No. C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities” showed a good stability of clopyralid residues for up to 15 days of refrigerated storage for high water content.

## Specimen preparation

The specimens were prepared according to ANADIAG SOPs.

The sample was blended with dry ice and placed for at least 12 hours at  $T < -18^{\circ}\text{C}$  for sublimation of dry ice. The amount required by the analytical method (2 g) was weighed from this homogeneous matrix..

## Specimen analysis

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

Outline of ANADIAG method:

Residues of clopyralid and its conjugates are extracted and hydrolysed from samples by heating at  $60^{\circ}\text{C}$  for 3 hours with 2.5M KOH. After acidification with  $\text{H}_2\text{SO}_4$ , addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract is purified with a liquid-liquid partition. An aliquot of the upper layer is evaporated to dryness and the sample is reconstituted in 50:50, methanol/ $\text{H}_2\text{O}$  + 0.1% formic acid. Extracts are analysed by LC-MS/MS.

ANADIAG References (French version) of the method are

for the preparation and extraction of the samples: **SOP MP 718**

for the analysis of extracts and for the calibration: **SOP MA 1809**

## LOD

The limit of detection (LOD) was expressed as lowest calibration standard.

The LOD was 0.4 ng/mL for clopyralid in high water content (corresponding to 0.002 mg/kg for clopyralid and 0.003 mg/kg for clopyralid glycine).

## LOQ

The LOQ was 0.01 mg/kg for clopyralid and clopyralid glycine in high water content.

## Preparation of standard solutions

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

	Solvent	Concentration	Storage conditions	Expiry date (Preparation + ...)
Stock solution Clopyralid	Acetonitrile	$\approx 1$ mg/mL	Frozen	6 months
Stock solution Clopyralid glycine	Methanol	$\approx 1$ mg/mL	Frozen	6 months
Spiking solutions All analyte separately	Acetonitrile	$\approx 0.2, 2$ and $20$ $\mu\text{g/mL}$	Frozen	1 month
Intermediate calibration solutions Clopyralid <sup>(1)</sup>	Control extract	$\approx 200$ and $20$ ng/mL	Refrigerated	14 days
Matrix-matched Calibration solutions Clopyralid <sup>(1)</sup>	Control extract	$\approx 0.4$ to $24$ ng/mL	Refrigerated	14 days
Intermediate calibration solutions Clopyralid <sup>(2)</sup>	Methanol / water (50/50) + 0.1% formic acid	$\approx 200$ and $20$ ng/mL	Refrigerated	14 days
Calibration solution Clopyralid <sup>(2)</sup>	Methanol / water (50/50) + 0.1% formic acid	$\approx 0.4$ to $24$ ng/mL	Refrigerated	14 days

<sup>(1)</sup> For analysis of undiluted extracts

<sup>(2)</sup> For analysis of diluted extracts (dilution factor  $\geq 20$ )

## Calibration curves

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas of clopyralid obtained from chromatograms were plotted versus concentration and the

calibration functions were determined by least square fit.

Number and concentrations of standards used, as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve (r) should be  $\geq 0.990$  for the calibration to be acceptable with regression residuals randomly distributed.

All extracts analysed (after dilution when required) fell within the range of the standard curve.

### Fortification procedure

Fortifications were performed by adding known amounts of the spiking solutions to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

The spiked samples for roots and leaves with tops were done on untreated samples available at ANADIAG laboratory (ANADIAG sample No. S593 for whole plants, S595 for roots and S594 for leaves with tops). The absence of the analyte in these samples was checked within this study. The amount found was not detectable

Analytical Sample No.	Matrix	Fortification level (mg/kg)	Clopyralid % Recovery	Clopyralid glycine % Recovery	Extraction date
S593 01 AA	Whole plants	0.01	81.3%	-	07/02/2023
S593 01 BA	Whole plants	0.10	98.1%	-	08/02/2023
S593 01 CA	Whole plants	0.01	-	71.3%	08/02/2023
S593 01 DA	Whole plants	0.10	-	77.8%	07/02/2023
S593 01 EA d250	Whole plants	25	107.2%	-	15/02/2023
S593 01 FA d250	Whole plants	25	-	100.7%	15/02/2023
S594 01 AA	Leaves with tops	0.01	92.8%	-	09/02/2023
S594 01 BA	Leaves with tops	0.10	91.9%	-	10/02/2023
S594 01 CA	Leaves with tops	0.01	-	71.9%	10/02/2023
S594 01 DA	Leaves with tops	0.10	-	74.2%	09/02/2023
S594 01 EA d10	Leaves with tops	1.0	96.5%	-	15/02/2023
S594 01 FA d10	Leaves with tops	1.0	-	83.9%	15/02/2023
S595 01 AA	Roots	0.01	99.8%	-	13/02/2023
S595 01 BA	Roots	0.10	95.7%	-	14/02/2023
S595 01 CA	Roots	0.01	-	72.4%	14/02/2023
S595 01 DA	Roots	0.10	-	79.7%	13/02/2023
S595 01 EA D10	Roots	1.0	102.1%	-	17/02/2023
S595 01 FA D10	Roots	1.0	-	76.1%	17/02/2023

The recoveries of the spiked samples met with the acceptance criteria described in SANTE/2020/12830, Rev.1.

### Results

The analytical results obtained are summarized in the table below

**Table 1 TRIAL No. C2127 AN1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2127 01 01	C2127 AN1 / U1 / A	-	Whole plants	-	<b>NDR</b>
C2127 01 02	C2127 AN1 / T1 / A	<b>FAWORYT 300 SL</b>	Whole plants	0	<b>9.87</b>
C2127 01 03	C2127 AN1 / T2 / A	<b>FAWORYT 300 SL</b>	Whole plants	7	<b>0.69</b>
C2127 01 04	C2127 AN1 / T3 / A	<b>FAWORYT 300 SL</b>	Whole plants	23	<b>0.09</b>
C2127 01 05	C2127 AN1 / T4R / A	<b>FAWORYT 300 SL</b>	Roots	42	<b>0.44</b>
C2127 01 06	C2127 AN1 / T4L / A	<b>FAWORYT 300 SL</b>	Leaves with tops	42	<b>0.52</b>
C2127 01 07	C2127 AN1 / UHR / A	-	Roots	-	<b>NDR</b>
C2127 01 08	C2127 AN1 / UHL / A	-	Leaves with tops	-	<b>NDR</b>
C2127 01 09	C2127 AN1 / THR / A	<b>FAWORYT 300 SL</b>	Roots	132	<b>0.15</b>
C2127 01 10	C2127 AN1 / THL / A	<b>FAWORYT 300 SL</b>	Leaves with tops	132	<b>0.20</b>

DAA: Days After Application

NDR: No detectable residues (residues below the limit of detection)

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

#### **A 2.1.3.1.1.3 Study 3**

Reference:	KCA 6.3/03
Report	Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Sugar Beets Following One Foliar application with FAWORYT 300 SL under Field Conditions in Northern Europe in 2022, M. Lefebvre 2023, C2128, Anadiag, France
Guideline(s):	Regulation (EC) No. 1107/2009 Regulation (EU) No. 283/2013 and 284/2013 2004/10/EC GLP Directive OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021 SANTE/2019/12752 - Technical guidelines on data requirements for setting Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin. SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.
Deviations:	No
GLP:	Yes
Acceptability:	Yes

#### **Objective of the study**

The objective of the study was to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Sugar beet raw agricultural commodity (RAC) after one foliar application of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.5 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at 1 site in Northern Europe. The trial was sampled at harvest.

One plot was treated once with FAWORYT 300 SL at BBCH 14, at the application rate of 0.5 L/ha (150

g clopyralid/ha).

One plot remained untreated.

Sampling was performed at normal commercial harvest (BBCH 49) in treated and untreated plots.

Clopyralid (Sum of clopyralid, its salts and conjugates) residues were analysed in samples harvested during the field phase..

### Field phase description

The objective of the study was to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Sugar beet raw agricultural commodity (RAC) after one foliar application of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.5 L/ha.

The following pattern was designed for the treatments and the samplings:

#### 1.1.1.1 Application details

Plot	Test Item	App. No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	<b>FAWORYT 300 SL</b>	T1	BBCH 14	0.5 L/ha	150 g/ha	200-300 L/ha (±10%)

#### 1.1.1.2 Sampling Details

##### Residue at harvest trial

Sampling event	Plot	Timing	Matrix	Min. Sample size
<b>S1</b>	U, T	NCH BBCH 49	Roots	2 kg, from min. 12 plants
			Leaves with tops	1 kg, from min. 12 plants

NCH: Normal Commercial harvest

### Location of the trial

The trial was performed on soil type and under cultural practices typical for sugar beet production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Type of trial	Crop	European area	Region, Country
1	<b>C2128 BW1</b>	Audrey MEYER	RH	Sugar beet	North	Baden-Württemberg, Germany

RH: Residues at harvest





#### Identity and composition of the test item(s):

##### Test item

<b>Trade or Code Name</b>	<b>FAWORYT 300 SL</b>
<b>Active substance (a.s.)</b>	Clopyralid (as clopyralid monoethanolamine salt)
<b>Formulation type</b>	SL
<b>CAS Number</b>	[1702-17-6] ([57754-85-5])
<b>Nominal content of a.s.</b>	300 g/L (expressed as clopyralid)
<b>Batch number*</b>	202203001
<b>Actual content *</b>	302.2 g/L (expressed as clopyralid)
<b>Expiry date*</b>	11/03/2025

#### General Information on the trial

##### Crop and soil Information

##### 1.2.2 Crop and soil Information

Trial No.	Crop	Variety	Crop density (plants/ha)	Sowing / Planting date	Soil type	pH	Organic matter (%)
C2128 BW1	Sugar beet	Cameleon	≈ 148 148	19/03/2022	Clay loam	< 7	2

#### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (m)	Pressure (bars)
C2128 BW1	PULVEXPER	Flat fan	Teejet XR 110 015 VS	3	9	0.33	1.9



### Summary of the actual application(s) data

Trial No.	Plot	Application No.	Active substance rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2128 BW1	T	1	136.7	-8.9	273	11/05/2022	14

### Sampling of specimens

#### Sampling summary

Trial No	Sampling	Actual Date	Actual timing	Actual Growth Stage (BBCH)
C2128 BW1	1	19/10/2022	161 DAA, NCH	49

NCH: Normal commercial harvest

DAA: Days after application

### ANALYTICAL PHASE

The objective of the analytical phase was to determine the residue levels of clopyralid in samples harvested during the field phase.

#### Experimental details

##### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trial.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

#### TRIAL No. C2128 BW1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2128 01 01	C2128 BW1 / UHR / A	19/10/2022	17/02/2023	121	18/02/2023	1
C2128 01 02	C2128 BW1 / UHL / A	19/10/2022	20/02/2023	124	21/02/2023	1
C2128 01 03	C2128 BW1 / THR / A	19/10/2022	17/02/2023	121	18/02/2023	1
C2128 01 04	C2128 BW1 / THL / A	19/10/2022	20/02/2023	124	21/02/2023	1

\*Frozen storage time of samples from sampling to extraction (days)

\*\*Refrigerated storage time of final extracts, from extraction to analysis (days)

### Storage stability of specimens

Specimens were stored frozen for no more than 124 days from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in commodities with high water, high oil, high acid and dry/high starch content (EFSA Journal Volume19, Issue1, January 2021, e06389).

### Storage stability of extracts

After extraction, samples were stored refrigerated and analysed after maximum 1 day.

Results of storage stability of extracts in ANADIAG validation study No. C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities” showed a good stability of clopyralid residues for up to 15 days of refrigerated storage for high water content.

### Specimen preparation

The specimens were prepared according to ANADIAG SOPs.

The sample was blended with dry ice and placed for at least 12 hours at  $T < -18^{\circ}\text{C}$  for sublimation of dry ice. The amount required by the analytical method (2 g) was weighed from this homogeneous matrix.

### Specimen analysis

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

Outline of ANADIAG method:

Residues of clopyralid and its conjugates are extracted and hydrolysed from samples by heating at  $60^{\circ}\text{C}$  for 3 hours with 2.5M KOH. After acidification with  $\text{H}_2\text{SO}_4$ , addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract is purified with a liquid-liquid partition. An aliquot of the upper layer is evaporated to dryness and the sample is reconstituted in 50:50, methanol/ $\text{H}_2\text{O}$  + 0.1% formic acid. Extracts are analysed by LC-MS/MS.

ANADIAG References (French version) of the method are

for the preparation and extraction of the samples: **SOP MP 718**

for the analysis of extracts and for the calibration: **SOP MA 1809**

### LOD

### LOD

The limit of detection (LOD) was expressed as lowest calibration standard.

The LOD was 0.4 ng/mL for clopyralid in high water content (corresponding to 0.002 mg/kg for clopyralid and 0.003 mg/kg for clopyralid glycine).

### LOQ

The LOQ was 0.01 mg/kg for clopyralid and clopyralid glycine in high water content.

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

	Solvent	Concentration	Storage conditions	Expiry date (Preparation + ...)
Stock solution Clopyralid	Acetonitrile	$\approx 1 \text{ mg/mL}$	Frozen	6 months
Stock solution Clopyralid glycine	Methanol	$\approx 1 \text{ mg/mL}$	Frozen	6 months
Spiking solutions All analyte separately	Acetonitrile	$\approx 0.2$ and $2 \text{ }\mu\text{g/mL}$	Frozen	1 month
Intermediate calibration solutions Clopyralid	Control extract	$\approx 200$ and $20 \text{ ng/mL}$	Refrigerated	14 days
Matrix-matched Calibration solutions Clopyralid	Control extract	$\approx 0.4$ to $24 \text{ ng/mL}$	Refrigerated	14 days

### Calibration curves

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas of clopyralid obtained from chromatograms were plotted versus concentration and the calibration functions were determined by least square fit.

Number and concentrations of standards used, as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve ( $r$ ) should be  $\geq 0.990$  for the calibration to be acceptable with regression residuals randomly distributed.

All extracts analysed (after dilution when required) fell within the range of the standard curve.

### Fortification procedure

Fortifications were performed by adding known amounts of the spiking solutions to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

The spiked samples for roots and leaves with tops were done on untreated samples available at ANADIAG laboratory (ANADIAG sample No. S597 and S595 for roots and S598 for leaves with tops). The absence of the analyte in these samples was checked within this study. The amount found was not detectable

Analytical Sample No.	Matrix	Fortification level (mg/kg)	Clopyralid % Recovery	Clopyralid glycine % Recovery	Extraction date
S597 01 AA	Roots	0.01	111.2%	-	17/02/2023
S597 01 BA	Roots	0.10	108.6%	-	17/02/2023
S595 01 EA D10	Roots	1.0	102.1%	-	17/02/2023
S597 01 CA	Roots	0.01	-	86.1%	17/02/2023
S597 01 DA	Roots	0.10	-	79.8%	17/02/2023
S595 01 FA D10	Roots	1.0	-	76.1%	17/02/2023
S598 01 AA	Leaves with tops	0.01	115.6%	-	20/02/2023
S598 01 BA D10	Leaves with tops	1.0	91.7%	-	20/02/2023
S598 01 CA	Leaves with tops	0.01	-	78.9%	20/02/2023
S598 01 DA D10	Leaves with tops	1.0	-	94.6%	20/02/2023

The recoveries of the spiked samples met with the acceptance criteria described in SANTE/2020/12830, Rev.1.

## Results

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2128 BW1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2128 01 01	C2128 BW1 / UHR / A	-	Roots	-	NDR
C2128 01 02	C2128 BW1 / UHL / A	-	Leaves with tops	-	NDR
C2128 01 03	C2128 BW1 / THR / A	FAWORYT 300 SL	Roots	161	0.14
C2128 01 04	C2128 BW1 / THL / A	FAWORYT 300 SL	Leaves with tops	161	0.25

DAA: Days After Application

NDR: No detectable residues (residues below the limit of detection)

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

### A 2.1.3.1.1.4 Study 4

Reference: KCA 6.3/04

Report Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Sugar Beets Following One Foliar application with FAWORYT 300 SL under Field Conditions in Northern Europe in 2022, M. Lefebvre 2023, C2129, Anadiag, France

Guideline(s): Regulation (EC) No. 1107/2009  
Regulation (EU) No. 283/2013 and 284/2013  
2004/10/EC GLP Directive

OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021  
SANTE/2019/12752 - Technical guidelines on data requirements for setting Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin.  
SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes  
OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.

Deviations: No

GLP: Yes

Acceptability: Yes

### Objective of the study

The objective of the study was to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Sugar beet raw agricultural commodity (RAC) after one foliar application of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.5 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at 1 site in Northern Europe. The trial was sampled at harvest.

One plot was treated once with FAWORYT 300 SL at BBCH 14, at the application rate of 0.5 L/ha (150 g clopyralid/ha).

One plot remained untreated.

Sampling was performed at normal commercial harvest (BBCH 49) in treated and untreated plots.

Clopyralid (Sum of clopyralid, its salts and conjugates) residues were analysed in samples harvested during the field phase.

### Field phase description

The objective of the study was to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Sugar beet raw agricultural commodity (RAC) after one foliar application of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.5 L/ha.

The following pattern was designed for the treatments and the samplings:

#### 1.1.1.1 Application details

Plot	Test Item	App. No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	FAWORYT 300 SL	T1	BBCH 14	0.5 L/ha	150 g/ha	200-300 L/ha (±10%)

#### 1.1.1.2 Sampling Details

##### Residue at harvest trial

Sampling event	Plot	Timing	Matrix	Min. Sample size
S1	U, T	NCH BBCH 49	Roots	2 kg, from min. 12 plants
			Leaves with tops	1 kg, from min. 12 plants

NCH: Normal Commercial harvest

### Location of the trial

The trial was performed on soil type and under cultural practices typical for sugar beet production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Type of trial	Crop	European area	Region, Country
1	C2129 ND1	Rémi DUTERTE	RH	Sugar beet	North	Hauts-de-France, France

RH: Residues at harvest



#### Identity and composition of the test item(s):

##### Test item

Trade or Code Name	FAWORYT 300 SL
Active substance (a.s.)	Clopyralid (as clopyralid monoethanolamine salt)
Formulation type	SL
CAS Number	[1702-17-6] ([57754-85-5])
Nominal content of a.s.	300 g/L (expressed as clopyralid)
Batch number*	202203001
Actual content *	302.2 g/L (expressed as clopyralid)
Expiry date*	11/03/2025

#### General Information on the trial

##### Crop and soil Information

Trial No.	Crop	Variety	Crop density (plants/ha)	Sowing / Planting date	Soil type	pH	Organic matter (%)
C2129 ND1	Sugar beet	Calledia	≈ 123 457	28/03/2022	Clay loam	7	2.2

#### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (m)	Pressure (bars)
C2129 ND1	PULVEXPER	Flat fan	Teejet XR 110 015 VS	3	9	0.33	2

#### Summary of the actual application(s) data

Trial No.	Plot	Application No.	Active substance rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2129 ND1	T	1	150.0	0.0	300	12/05/2022	14

#### Sampling of specimens

Trial No	Sampling	Actual Date	Actual timing	Actual Growth Stage (BBCH)
C2129 ND1	1	05/09/2022	116 DAA, NCH	49

NCH: Normal commercial harvest

DAA: Days after application

### ANALYTICAL PHASE

The objective of the analytical phase was to determine the residue levels of clopyralid in samples harvested during the field phase.

#### Experimental details

##### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trial.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table:

##### TRIAL No. C2129 ND1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2129 01 01	C2129 ND1 / UHR / A	05/09/2022	17/02/2023	165	18/02/2023	1
C2129 01 02	C2129 ND1 / UHL / A	05/09/2022	20/02/2023	168	21/02/2023	1
C2129 01 03	C2129 ND1 / THR / A	05/09/2022	17/02/2023	165	18/02/2023	1
C2129 01 04	C2129 ND1 / THL / A	05/09/2022	20/02/2023	168	21/02/2023	1

\*Frozen storage time of samples from sampling to extraction (days)

\*\*Refrigerated storage time of final extracts, from extraction to analysis (days)

#### Storage stability of specimens

Specimens were stored frozen for no more than 168 days from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in commodities with high water, high oil, high acid and dry/high starch content (EFSA Journal Volume19, Issue1, January 2021, e06389).

#### Storage stability of extracts

After extraction, samples were stored refrigerated and analysed after maximum 1 day.

Results of storage stability of extracts in ANADIAG validation study No. C2135 entitled “Validation of



the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities” showed a good stability of clopyralid residues for up to 15 days of refrigerated storage for high water content.

### Specimen preparation

The specimens were prepared according to ANADIAG SOPs.

The sample was blended with dry ice and placed for at least 12 hours at  $T < -18^{\circ}\text{C}$  for sublimation of dry ice. The amount required by the analytical method (2 g) was weighed from this homogeneous matrix.

### Specimen analysis

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

Outline of ANADIAG method:

Residues of clopyralid and its conjugates are extracted and hydrolysed from samples by heating at  $60^{\circ}\text{C}$  for 3 hours with 2.5M KOH. After acidification with  $\text{H}_2\text{SO}_4$ , addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract is purified with a liquid-liquid partition. An aliquot of the upper layer is evaporated to dryness and the sample is reconstituted in 50:50, methanol/ $\text{H}_2\text{O}$  + 0.1% formic acid. Extracts are analysed by LC-MS/MS.

ANADIAG References (French version) of the method are

for the preparation and extraction of the samples: **SOP MP 718**

for the analysis of extracts and for the calibration: **SOP MA 1809**

### LOD

The limit of detection (LOD) was expressed as lowest calibration standard.

The LOD was 0.4 ng/mL for clopyralid in high water content (corresponding to 0.002 mg/kg for clopyralid and 0.003 mg/kg for clopyralid glycine).

### LOQ

The LOQ was 0.01 mg/kg for clopyralid and clopyralid glycine in high water content.

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

	Solvent	Concentration	Storage conditions	Expiry date (Preparation + ...)
Stock solution Clopyralid	Acetonitrile	$\approx 1$ mg/mL	Frozen	6 months
Stock solution Clopyralid glycine	Methanol	$\approx 1$ mg/mL	Frozen	6 months
Spiking solutions All analyte separately	Acetonitrile	$\approx 0.2$ and $2$ $\mu\text{g/mL}$	Frozen	1 month
Intermediate calibration solutions Clopyralid	Control extract	$\approx 200$ and $20$ ng/mL	Refrigerated	14 days
Matrix-matched Calibration solutions Clopyralid	Control extract	$\approx 0.4$ to $24$ ng/mL	Refrigerated	14 days

### Calibration curves

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas of clopyralid obtained from chromatograms were plotted versus concentration and the calibration functions were determined by least square fit.

Number and concentrations of standards used, as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve ( $r$ ) should be  $\geq 0.990$  for the

calibration to be acceptable with regression residuals randomly distributed.  
All extracts analysed (after dilution when required) fell within the range of the standard curve.

### Fortification procedure

Fortifications were performed by adding known amounts of the spiking solutions to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

The spiked samples for roots and leaves with tops were done on untreated samples available at ANADIAG laboratory (ANADIAG sample No. S597 and S595 for roots and S598 for leaves with tops). The absence of the analyte in these samples was checked within this study. The amount found was not detectable

Analytical Sample No.	Matrix	Fortification level (mg/kg)	Clopyralid % Recovery	Clopyralid glycine % Recovery	Extraction date
S597 01 AA	Roots	0.01	111.2%	-	17/02/2023
S597 01 BA	Roots	0.10	108.6%	-	17/02/2023
S595 01 EA D10	Roots	1.0	102.1%	-	17/02/2023
S597 01 CA	Roots	0.01	-	86.1%	17/02/2023
S597 01 DA	Roots	0.10	-	79.8%	17/02/2023
S595 01 FA D10	Roots	1.0	-	76.1%	17/02/2023
S598 01 AA	Leaves with tops	0.01	115.6%	-	20/02/2023
S598 01 BA D10	Leaves with tops	1.0	91.7%	-	20/02/2023
S598 01 CA	Leaves with tops	0.01	-	78.9%	20/02/2023
S598 01 DA D10	Leaves with tops	1.0	-	94.6%	20/02/2023

The recoveries of the spiked samples met with the acceptance criteria described in SANTE/2020/12830, Rev.1.

### Results

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2129 ND1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2129 01 01	C2129 ND1 / UHR / A	-	Roots	-	NDR
C2129 01 02	C2129 ND1 / UHL / A	-	Leaves with tops	-	NDR
C2129 01 03	C2129 ND1 / THR / A	FAWORYT 300 SL	Roots	116	0.09
C2129 01 04	C2129 ND1 / THL / A	FAWORYT 300 SL	Leaves with tops	116	0.09

DAA: Days After Application

NDR: No detectable residues (residues below the limit of detection)

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

### A 2.1.3.1.1.5 Study 5

Reference:	KCA 6.3/05
Report	Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates)



Residues in Sugar Beets Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022, M. Lefebvre 2023, C2130, Anadiag, France

Guideline(s):	Regulation (EC) No. 1107/2009 Regulation (EU) No. 283/2013 and 284/2013 2004/10/EC GLP Directive OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021 SANTE/2019/12752 - Technical guidelines on data requirements for setting Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin. SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.
Deviations:	No
GLP:	Yes
Acceptability:	Yes

### Objective of the study

The objective of the study was to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Sugar beet raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.5 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at 1 site in Northern Europe. The trial was sampled frequently to monitor the decline of residues shortly after the treatment.

One plot was treated once with CHR/H/CPD 300 SL at BBCH 14, at the application rate of 0.5 L/ha (150 g clopyralid/ha).

One plot remained untreated.

Sampling was performed at 0 DBA (Day before Application) in untreated plot, 0 DAA (Day after application) in treated plot, 7 DAA; 22 DAA, 42 DAA in treated plot. Final sampling was performed at normal commercial harvest (BBCH 49) in treated and untreated plots.

Clopyralid (Sum of clopyralid, its salts and conjugates) residues were analysed in samples harvested during the field phase.

### Field phase description

The objective of the study was to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Sugar beet raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.5 L/ha.

The following pattern was designed for the treatments and the samplings:

#### 1.1.1.1 Application details

Plot	Test Item	App. No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	CHR/H/CPD 300 SL	T1	BBCH 14	0.5 L/ha	150 g/ha	200-300 L/ha (±10%)

### 1.1.1.2 Sampling Details

#### Decline curve trial

Sampling event	Plot	Timing	Matrix	Min. Sample size
S1	U	0 DBA	Whole plants	0.1 kg and min. 12 plants
	T	0 DAA	Whole plants	0.1 kg and min. 12 plants
S2	T	7 ( $\pm$ 1) DAA	Whole plants	0.1 kg and min. 12 plants
S3	T	21 ( $\pm$ 2) DAA	Whole plants	0.1 kg and min. 12 plants
S4	T	40 ( $\pm$ 2) DAA	Roots	0.5 kg, from min. 12 plants
			Leaves with tops	0.5 kg, from min. 12 plants
S5	U, T	NCH BBCH 49	Roots	2 kg, from min. 12 plants
			Leaves with tops	1 kg, from min. 12 plants

DBA : Days before application

DAA : Days after application

NCH: Normal Commercial harvest

#### Location of the trial

The trial was performed on soil type and under cultural practices typical for sugar beet production and on a typical cultivar of the regional commercial production.



#### Identity and composition of the test item(s):

##### Test item

Trade or Code Name	CHR/H/CPD 300 SL
Active substance (a.s.)	Clopyralid

<b>Formulation type</b>	SL
<b>CAS Number</b>	[1702-17-6]
<b>Nominal content of a.s.</b>	300 g/L (expressed as clopyralid)
<b>Batch number*</b>	02/2018
<b>Actual content *</b>	30.18 %
<b>Expiry date*</b>	31/12/2022

## General Information on the trial

### Crop and soil Information

Trial No.	Crop	Variety	Crop density (plants/ha)	Sowing / Planting date	Soil type	pH	Organic matter (%)
C2130 HU1	Sugar beet	Conviso Smart	≈ 111 111	11/04/2022	Clay loam	7.9	2.21

### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (m)	Pressure (bars)
C2130 HU1	EUROPULVE	Flat fan	Albuz AVI ISO 110 015	3	9	0.33	3.5

### Summary of the actual application(s) data

Trial No.	Plot	Application No.	Active substance rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2130 HU1	T	1	165.8	+10.6*	332	16/05/2022	14

\* See deviation No.17/05/2022

### Sampling of specimens

Trial No	Sampling	Actual Date	Actual timing	Actual Growth Stage (BBCH)
C2130 HU1	1	16/05/2022	0 DBA / 0 DAA	14
	2	23/05/2022	7 DAA	18
	3	07/06/2022	22 DAA	35
	4	27/06/2022	42 DAA	38
	5	18/10/2022	155 DAA, NCH	49

DAA: Days after application

DBA: Day before application

NCH: Normal commercial harvest

## ANALYTICAL PHASE

The objective of the analytical phase was to determine the residue levels of clopyralid in samples harvested during the field phase.

### Experimental details

#### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trial.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table::

#### TRIAL No. C2130 HU1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2130 01 01	C2130 HU1 / U1 / A	16/05/2022	08/02/2023	268	11/02/2023	3
C2130 01 02	C2130 HU1 / T1 / A	16/05/2022	08/02/2023	268	16/02/2023	8
C2130 01 03	C2130 HU1 / T2 / A	23/05/2022	08/02/2023	261	16/02/2023	8
C2130 01 04	C2130 HU1 / T3 / A	07/06/2022	08/02/2023	246	16/02/2023	8
C2130 01 05	C2130 HU1 / T4R / A	27/06/2022	14/02/2023	232	18/02/2023	4
C2130 01 06	C2130 HU1 / T4L / A	27/06/2022	10/02/2023	228	16/02/2023	6
C2130 01 07	C2130 HU1 / UHR / A	18/10/2022	14/02/2023	119	17/02/2023	3
C2130 01 08	C2130 HU1 / UHL / A	18/10/2022	10/02/2023	115	11/02/2023	1
C2130 01 09	C2130 HU1 / THR / A	18/10/2022	14/02/2023	119	17/02/2023	3
C2130 01 10	C2130 HU1 / THL / A	18/10/2022	10/02/2023	115	11/02/2023	1

#### Storage stability of specimens

Specimens were stored frozen for no more than 268 days from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in commodities with high water, high oil, high acid and dry/high starch content (EFSA Journal Volume19, Issue1, January 2021, e06389).

#### Storage stability of extracts

After extraction, samples were stored refrigerated and analysed after maximum 8 days.

Results of storage stability of extracts in ANADIAG validation study No. C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities” showed a good stability of clopyralid residues for up to 15 days of refrigerated storage for high water content.

#### Specimen preparation

The specimens were prepared according to ANADIAG SOPs.

The sample was blended with dry ice and placed for at least 12 hours at  $T < -18^{\circ}\text{C}$  for sublimation of dry ice. The amount required by the analytical method (2 g) was weighed from this homogeneous matrix.

#### Specimen analysis

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

Outline of ANADIAG method:

Residues of clopyralid and its conjugates are extracted and hydrolysed from samples by heating at  $60^{\circ}\text{C}$  for 3 hours with 2.5M KOH. After acidification with  $\text{H}_2\text{SO}_4$ , addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract is purified with a liquid-liquid partition. An aliquot of the upper layer is evaporated to dryness and the sample is reconstituted in 50:50, methanol/ $\text{H}_2\text{O}$  + 0.1% formic acid. Extracts are analysed by LC-MS/MS.

ANADIAG References (French version) of the method are

for the preparation and extraction of the samples: **SOP MP 718**

for the analysis of extracts and for the calibration: **SOP MA 1809**

#### LOD

The limit of detection (LOD) was expressed as lowest calibration standard.

The LOD was 0.4 ng/mL for clopyralid in high water content (corresponding to 0.002 mg/kg for clopyralid and 0.003 mg/kg for clopyralid glycine).

#### LOQ

The LOQ was 0.01 mg/kg for clopyralid and clopyralid glycine in high water content.

## Preparation of standard solutions

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

	Solvent	Concentration	Storage conditions	Expiry date (Preparation + ...)
<b>Stock solution</b> <b>Clopyralid</b>	Acetonitrile	≈ 1 mg/mL	Frozen	6 months
<b>Stock solution</b> <b>Clopyralid glycine</b>	Methanol	≈ 1 mg/mL	Frozen	6 months
<b>Spiking solutions</b> <b>All analyte separately</b>	Acetonitrile	≈ 0.2, 2 and 20 µg/mL	Frozen	1 month
<b>Intermediate calibration solutions</b> <b>Clopyralid<sup>(1)</sup></b>	Control extract	≈ 200 and 20 ng/mL	Refrigerated	14 days
<b>Matrix-matched</b> <b>Calibration solutions</b> <b>Clopyralid<sup>(1)</sup></b>	Control extract	≈ 0.4 to 24 ng/mL	Refrigerated	14 days
<b>Intermediate calibration solutions</b> <b>Clopyralid<sup>(2)</sup></b>	Methanol / water (50/50) + 0.1% formic acid	≈ 200 and 20 ng/mL	Refrigerated	14 days
<b>Calibration solution</b> <b>Clopyralid<sup>(2)</sup></b>	Methanol / water (50/50) + 0.1% formic acid	≈ 0.4 to 24 ng/mL	Refrigerated	14 days

<sup>(1)</sup> For analysis of undiluted extracts

<sup>(2)</sup> For analysis of diluted extracts (dilution factor ≥ 20)

## Calibration curves

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas of clopyralid obtained from chromatograms were plotted versus concentration and the calibration functions were determined by least square fit.

Number and concentrations of standards used, as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve (r) should be ≥ 0.990 for the calibration to be acceptable with regression residuals randomly distributed.

All extracts analysed (after dilution when required) fell within the range of the standard curve.

## Fortification procedure

Fortifications were performed by adding known amounts of the spiking solutions to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

The spiked samples for roots and leaves with tops were done on untreated samples available at ANADIAG laboratory (ANADIAG sample No. S593 for whole plants, S595 for roots and S594 for leaves with tops). The absence of the analyte in these samples was checked within this study. The amount found was not detectable

Analytical Sample No.	Matrix	Fortification level (mg/kg)	Clopyralid % Recovery	Clopyralid glycine % Recovery	Extraction date
S593 01 AA	Whole plants	0.01	81.3%	-	07/02/2023
S593 01 BA	Whole plants	0.10	98.1%	-	08/02/2023
S593 01 CA	Whole plants	0.01	-	71.3%	08/02/2023
S593 01 DA	Whole plants	0.10	-	77.8%	07/02/2023
S593 01 EA d250	Whole plants	25	107.2%	-	15/02/2023
S593 01 FA d250	Whole plants	25	-	100.7%	15/02/2023
S594 01 AA	Leaves with tops	0.01	92.8%	-	09/02/2023
S594 01 BA	Leaves with tops	0.10	91.9%	-	10/02/2023
S594 01 CA	Leaves with tops	0.01	-	71.9%	10/02/2023
S594 01 DA	Leaves with tops	0.10	-	74.2%	09/02/2023
S594 01 EA d10	Leaves with tops	1.0	96.5%	-	15/02/2023
S594 01 FA d10	Leaves with tops	1.0	-	83.9%	15/02/2023
S595 01 AA	Roots	0.01	99.8%	-	13/02/2023
S595 01 BA	Roots	0.10	95.7%	-	14/02/2023
S595 01 CA	Roots	0.01	-	72.4%	14/02/2023
S595 01 DA	Roots	0.10	-	79.7%	13/02/2023
S595 01 EA D10	Roots	1.0	102.1%	-	17/02/2023
S595 01 FA D10	Roots	1.0	-	76.1%	17/02/2023

The recoveries of the spiked samples met with the acceptance criteria described in SANTE/2020/12830, Rev.1.

## Results

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2130 HU1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2130 01 01	C2130 HU1 / U1 / A	-	Whole plants	-	< LOQ
C2130 01 02	C2130 HU1 / T1 / A	CHR/H/CPD 300 SL	Whole plants	0	11.65
C2130 01 03	C2130 HU1 / T2 / A	CHR/H/CPD 300 SL	Whole plants	7	0.47
C2130 01 04	C2130 HU1 / T3 / A	CHR/H/CPD 300 SL	Whole plants	22	0.70
C2130 01 05	C2130 HU1 / T4R / A	CHR/H/CPD 300 SL	Roots	42	0.71
C2130 01 06	C2130 HU1 / T4L / A	CHR/H/CPD 300 SL	Leaves with tops	42	0.23
C2130 01 07	C2130 HU1 / UHR / A	-	Roots	-	NDR
C2130 01 08	C2130 HU1 / UHL / A	-	Leaves with tops	-	NDR
C2130 01 09	C2130 HU1 / THR / A	CHR/H/CPD 300 SL	Roots	155	0.06
C2130 01 10	C2130 HU1 / THL / A	CHR/H/CPD 300 SL	Leaves with tops	155	0.07

DAA: Days After Application

NDR: No detectable residues (residues below the limit of detection)

< LOQ: Residues between LOD and LOQ

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

### A 2.1.3.1.1.6 Study 6

Reference: KCA 6.3/06

Report: Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Sugar Beets Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022, M. Lefebvre 2023, C2131, Anadiag, France



Guideline(s):	Regulation (EC) No. 1107/2009 Regulation (EU) No. 283/2013 and 284/2013 2004/10/EC GLP Directive OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021 SANTE/2019/12752 - Technical guidelines on data requirements for setting Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin. SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.
Deviations:	No
GLP:	Yes
Acceptability:	Yes

### Objective of the study

The objective of the study was to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Sugar beet raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.5 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at 1 site in Northern Europe. The trial was sampled frequently to monitor the decline of residues shortly after the treatment.

One plot was treated once with CHR/H/CPD 300 SL at BBCH 14, at the application rate of 0.5 L/ha (150 g clopyralid/ha).

One plot remained untreated.

Sampling was performed at 0 DBA (Day before Application) in untreated plot, 0 DAA (Day after application) in treated plot, 7 DAA; 19 DAA, 39 DAA in treated plot. Final sampling was performed at normal commercial harvest (BBCH 49) in treated and untreated plots.

Clopyralid (Sum of clopyralid, its salts and conjugates) residues were analysed in samples harvested during the field phase.

### Field phase description

The objective of the study was to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Sugar beet raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.5 L/ha.

The following pattern was designed for the treatments and the samplings:

#### 1.1.1.1 Application details

Plot	Test Item	App. No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	CHR/H/CPD 300 SL	T1	BBCH 14	0.5 L/ha	150 g/ha	200-300 L/ha (±10%)

#### Decline curve trial

Sampling event	Plot	Timing	Matrix	Min. Sample size
<b>S1</b>	U	0 DBA	Whole plants	0.1 kg and min. 12 plants
	T	0 DAA	Whole plants	0.1 kg and min. 12 plants
<b>S2</b>	T	7 ( $\pm$ 1) DAA	Whole plants	0.1 kg and min. 12 plants
<b>S3</b>	T	21 ( $\pm$ 2) DAA	Whole plants	0.1 kg and min. 12 plants
<b>S4</b>	T	40 ( $\pm$ 2) DAA	Roots	0.5 kg, from min. 12 plants
			Leaves with tops	0.5 kg, from min. 12 plants
<b>S5</b>	U, T	NCH BBCH 49	Roots	2 kg, from min. 12 plants
			Leaves with tops	1 kg, from min. 12 plants

DBA : Days before application

DAA : Days after application

NCH: Normal Commercial harvest

#### Location of the trial

The trial was performed on soil type and under cultural practices typical for sugar beet production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Type of trial	Crop	European area	Region, Country
<b>1</b>	<b>C2131 CZ1</b>	Iva SIMEK	DC	Sugar beet	North	Pardubice, Czech Republic

DC: Decline curve





#### Identity and composition of the test item(s):

##### Test item

<b>Trade or Code Name</b>	<b>CHR/H/CPD 300 SL</b>
<b>Active substance (a.s.)</b>	Clopyralid
<b>Formulation type</b>	SL
<b>CAS Number</b>	[1702-17-6]
<b>Nominal content of a.s.</b>	300 g/L (expressed as clopyralid)
<b>Batch number*</b>	02/2018
<b>Actual content *</b>	30.18 %
<b>Expiry date*</b>	31/12/2022

#### General Information on the trial

##### Crop and soil Information

Trial No.	Crop	Variety	Crop density (plants/ha)	Sowing / Planting date	Soil type	pH	Organic matter (%)
<b>C2131 CZ1</b>	Sugar beet	Convigo smart	100 000	29/03/2022	Clay loam	5.9	2.0

#### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (m)	Pressure (bars)
<b>C2131 CZ1</b>	PULVEXPER	Flat fan	Teejet XR 110 015 VS	3	9	0.33	2

### Summary of the actual application(s) data

Trial No.	Plot	Application No.	Active substance rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2131 CZ1	T	1	148.0	-1.3	247	09/05/2022	14

### Sampling of specimens

Trial No	Sampling	Actual Date	Actual timing	Actual Growth Stage (BBCH)
C2131 CZ1	1	09/05/2022	0 DBA / 0 DAA	14
	2	16/05/2022	7 DAA	16-17
	3	28/05/2022	19 DAA	17
	4	17/06/2022	39 DAA	37
	5	29/09/2022	143 DAA, NCH	49

DAA: Days after application

DBA: Day before application

NCH: Normal commercial harvest

### ANALYTICAL PHASE

The objective of the analytical phase was to determine the residue levels of clopyralid in samples harvested during the field phase.

#### Experimental details

##### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trial.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table::

#### TRIAL No. C2131 CZ1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2131 01 01	C2131 CZ1 / U1 / A	09/05/2022	08/02/2023	275	11/02/2023	3
C2131 01 02	C2131 CZ1 / T1 / A	09/05/2022	08/02/2023	275	16/02/2023	8
C2131 01 03	C2131 CZ1 / T2 / A	16/05/2022	08/02/2023	268	16/02/2023	8
C2131 01 04	C2131 CZ1 / T3 / A	28/05/2022	08/02/2023	256	16/02/2023	8
C2131 01 05	C2131 CZ1 / T4R / A	17/06/2022	14/02/2023	242	18/02/2023	4
C2131 01 06	C2131 CZ1 / T4L / A	17/06/2022	10/02/2023	238	16/02/2023	6
C2131 01 07	C2131 CZ1 / UHR / A	29/09/2022	14/02/2023	138	17/02/2023	3
C2131 01 08	C2131 CZ1 / UHL / A	29/09/2022	10/02/2023	134	11/02/2023	1
C2131 01 09	C2131 CZ1 / THR / A	29/09/2022	14/02/2023	138	17/02/2023	3
C2131 01 10	C2131 CZ1 / THL / A	29/09/2022	10/02/2023	134	11/02/2023	1

### **Storage stability of specimens**

Specimens were stored frozen for no more than 275 days from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in commodities with high water, high oil, high acid and dry/high starch content (EFSA Journal Volume19, Issue1, January 2021, e06389).

### **Storage stability of extracts**

After extraction, samples were stored refrigerated and analysed after maximum 8 days.

Results of storage stability of extracts in ANADIAG validation study No. C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities” showed a good stability of clopyralid residues for up to 15 days of refrigerated storage for high water content.

### **Specimen preparation**

The specimens were prepared according to ANADIAG SOPs.

The sample was blended with dry ice and placed for at least 12 hours at  $T < -18^{\circ}\text{C}$  for sublimation of dry ice. The amount required by the analytical method (2 g) was weighed from this homogeneous matrix..

### **Specimen analysis**

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

Outline of ANADIAG method:

Residues of clopyralid and its conjugates are extracted and hydrolysed from samples by heating at  $60^{\circ}\text{C}$  for 3 hours with 2.5M KOH. After acidification with  $\text{H}_2\text{SO}_4$ , addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract is purified with a liquid-liquid partition. An aliquot of the upper layer is evaporated to dryness and the sample is reconstituted in 50:50, methanol/ $\text{H}_2\text{O}$  + 0.1% formic acid. Extracts are analysed by LC-MS/MS.

ANADIAG References (French version) of the method are

for the preparation and extraction of the samples: **SOP MP 718**

for the analysis of extracts and for the calibration: **SOP MA 1809**

### **LOD**

#### **LOD**

The limit of detection (LOD) was expressed as lowest calibration standard.

The LOD was 0.4 ng/mL for clopyralid in high water content (corresponding to 0.002 mg/kg for clopyralid and 0.003 mg/kg for clopyralid glycine).

#### **LOQ**

The LOQ was 0.01 mg/kg for clopyralid and clopyralid glycine in high water content.

#### **Preparation of standard solutions**

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

	Solvent	Concentration	Storage conditions	Expiry date (Preparation + ...)
<b>Stock solution Clopyralid</b>	Acetonitrile	≈ 1 mg/mL	Frozen	6 months
<b>Stock solution Clopyralid glycine</b>	Methanol	≈ 1 mg/mL	Frozen	6 months
<b>Spiking solutions All analyte separately</b>	Acetonitrile	≈ 0.2, 2 and 20 µg/mL	Frozen	1 month
<b>Intermediate calibration solutions Clopyralid<sup>(1)</sup></b>	Control extract	≈ 200 and 20 ng/mL	Refrigerated	14 days
<b>Matrix-matched Calibration solutions Clopyralid<sup>(1)</sup></b>	Control extract	≈ 0.4 to 24 ng/mL	Refrigerated	14 days
<b>Intermediate calibration solutions Clopyralid<sup>(2)</sup></b>	Methanol / water (50/50) + 0.1% formic acid	≈ 200 and 20 ng/mL	Refrigerated	14 days
<b>Calibration solution Clopyralid<sup>(2)</sup></b>	Methanol / water (50/50) + 0.1% formic acid	≈ 0.4 to 24 ng/mL	Refrigerated	14 days

<sup>(1)</sup> For analysis of undiluted extracts

<sup>(2)</sup> For analysis of diluted extracts (dilution factor ≥ 20)

### Calibration curves

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas of clopyralid obtained from chromatograms were plotted versus concentration and the calibration functions were determined by least square fit.

Number and concentrations of standards used, as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve (r) should be ≥ 0.990 for the calibration to be acceptable with regression residuals randomly distributed.

All extracts analysed (after dilution when required) fell within the range of the standard curve.

### Fortification procedure

Fortifications were performed by adding known amounts of the spiking solutions to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

The spiked samples for roots and leaves with tops were done on untreated samples available at ANADIAG laboratory (ANADIAG sample No. S593 for whole plants, S595 for roots and S594 for leaves with tops). The absence of the analyte in these samples was checked within this study. The amount found was not detectable

Analytical Sample No.	Matrix	Fortification level (mg/kg)	Clopyralid % Recovery	Clopyralid glycine % Recovery	Extraction date
S593 01 AA	Whole plants	0.01	81.3%	-	07/02/2023
S593 01 BA	Whole plants	0.10	98.1%	-	08/02/2023
S593 01 CA	Whole plants	0.01	-	71.3%	08/02/2023
S593 01 DA	Whole plants	0.10	-	77.8%	07/02/2023
S593 01 EA d250	Whole plants	25	107.2%	-	15/02/2023
S593 01 FA d250	Whole plants	25	-	100.7%	15/02/2023
S594 01 AA	Leaves with tops	0.01	92.8%	-	09/02/2023
S594 01 BA	Leaves with tops	0.10	91.9%	-	10/02/2023
S594 01 CA	Leaves with tops	0.01	-	71.9%	10/02/2023
S594 01 DA	Leaves with tops	0.10	-	74.2%	09/02/2023
S594 01 EA d10	Leaves with tops	1.0	96.5%	-	15/02/2023
S594 01 FA d10	Leaves with tops	1.0	-	83.9%	15/02/2023
S595 01 AA	Roots	0.01	99.8%	-	13/02/2023
S595 01 BA	Roots	0.10	95.7%	-	14/02/2023
S595 01 CA	Roots	0.01	-	72.4%	14/02/2023
S595 01 DA	Roots	0.10	-	79.7%	13/02/2023
S595 01 EA D10	Roots	1.0	102.1%	-	17/02/2023
S595 01 FA D10	Roots	1.0	-	76.1%	17/02/2023

The recoveries of the spiked samples met with the acceptance criteria described in SANTE/2020/12830, Rev.1.

## Results

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2131 CZ1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2131 01 01	C2131 CZ1 / U1 / A	-	Whole plants	-	NDR
C2131 01 02	C2131 CZ1 / T1 / A	CHR/H/CPD 300 SL	Whole plants	0	9.68
C2131 01 03	C2131 CZ1 / T2 / A	CHR/H/CPD 300 SL	Whole plants	7	1.65
C2131 01 04	C2131 CZ1 / T3 / A	CHR/H/CPD 300 SL	Whole plants	19	1.08
C2131 01 05	C2131 CZ1 / T4R / A	CHR/H/CPD 300 SL	Roots	39	0.24
C2131 01 06	C2131 CZ1 / T4L / A	CHR/H/CPD 300 SL	Leaves with tops	39	0.47
C2131 01 07	C2131 CZ1 / UHR / A	-	Roots	-	NDR
C2131 01 08	C2131 CZ1 / UHL / A	-	Leaves with tops	-	NDR
C2131 01 09	C2131 CZ1 / THR / A	CHR/H/CPD 300 SL	Roots	143	< LOQ
C2131 01 10	C2131 CZ1 / THL / A	CHR/H/CPD 300 SL	Leaves with tops	143	0.01

DAA: Days After Application

NDR: No detectable residues (residues below the limit of detection)

< LOQ: Residues between LOD and LOQ

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

### A 2.1.3.1.1.7 Study 7

Reference:	KCA 6.3/07
Report	Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Sugar Beets Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022, M. Lefebvre 2023, C2132, Anadiag, France
Guideline(s):	Regulation (EC) No. 1107/2009 Regulation (EU) No. 283/2013 and 284/2013 2004/10/EC GLP Directive OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021 SANTE/2019/12752 - Technical guidelines on data requirements for setting Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin. SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.
Deviations:	No
GLP:	Yes
Acceptability:	Yes

### Objective of the study

The objective of the study was to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Sugar beet raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.5 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at 1 site in Northern Europe. The trial was sampled frequently to monitor the decline of residues shortly after the treatment.

One plot was treated once with CHR/H/CPD 300 SL at BBCH 14-16, at the application rate of 0.5 L/ha (150 g clopyralid/ha).

One plot remained untreated.

Sampling was performed at 0 DBA (Day before Application) in untreated plot, 0 DAA (Day after application) in treated plot, 6 DAA, 23 DAA, 40 DAA in treated plot. Final sampling was performed at normal commercial harvest (BBCH 49) in treated and untreated plots.

Clopyralid (Sum of clopyralid, its salts and conjugates) residues were analysed in samples harvested during the field phase.

### Field phase description

The objective of the study was to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Sugar beet raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.5 L/ha.

The following pattern was designed for the treatments and the samplings:

#### 1.1.1.1 Application details

Plot	Test Item	App. No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	CHR/H/CPD 300 SL	T1	BBCH 14	0.5 L/ha	150 g/ha	200-300 L/ha (±10%)



### 1.1.1.2 Sampling Details

#### Decline curve trial

Sampling event	Plot	Timing	Matrix	Min. Sample size
S1	U	0 DBA	Whole plants	0.1 kg and min. 12 plants
	T	0 DAA	Whole plants	0.1 kg and min. 12 plants
S2	T	7 ( $\pm$ 1) DAA	Whole plants	0.1 kg and min. 12 plants
S3	T	21 ( $\pm$ 2) DAA	Whole plants	0.1 kg and min. 12 plants
S4	T	40 ( $\pm$ 2) DAA	Roots	0.5 kg, from min. 12 plants
			Leaves with tops	0.5 kg, from min. 12 plants
S5	U, T	NCH BBCH 49	Roots	2 kg, from min. 12 plants
			Leaves with tops	1 kg, from min. 12 plants

DBA : Days before application

DAA : Days after application

NCH: Normal Commercial harvest

#### Location of the trial

The trial was performed on soil type and under cultural practices typical for sugar beet production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Type of trial	Crop	European area	Region, Country
1	C2132 PL1	Krzysztof NOWAK	DC	Sugar beet	North	Łódzkie, Poland

DC: Decline curve



#### Identity and composition of the test item(s):

##### Test item

<b>Trade or Code Name</b>	<b>CHR/H/CPD 300 SL</b>
<b>Active substance (a.s.)</b>	Clopyralid
<b>Formulation type</b>	SL
<b>CAS Number</b>	[1702-17-6]
<b>Nominal content of a.s.</b>	300 g/L (expressed as clopyralid)
<b>Batch number*</b>	02/2018
<b>Actual content *</b>	30.18 %
<b>Expiry date*</b>	31/12/2022

#### General Information on the trial

##### Crop and soil Information

Trial No.	Crop	Variety	Crop density	Sowing / Planting date	Soil type	pH	Organic matter (%)
C2132 PL1	Sugar beet	Kujavia	9.9 seeds/m <sup>2</sup>	15/04/2022	Sandy clay loam	6.5	3.0

#### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (m)	Pressure (bars)
C2132 PL1	EUROPULVE	Flat fan	Teejet XR 110 02 VS	3.0	9	0.33	3.0



#### Summary of the actual application(s) data

Trial No.	Plot	Application No.	Active substance rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2132 PL1	T	1	155.0	+3.3	310	18/05/2022	14-16*

\* BBCH 14 was the major crop stage in the field.

#### Sampling of specimens

Trial No	Sampling	Actual Date	Actual timing	Actual Growth Stage (BBCH)
C2132 PL1	1	18/05/2022	0 DBA / 0 DAA	14-16
	2	24/05/2022	6 DAA	16-17
	3	10/06/2022	23 DAA	33
	4	27/06/2022	40 DAA	39
	5	16/09/2022	121 DAA, NCH	49

DAA: Days after application

DBA: Day before application

NCH: Normal commercial harvest

#### ANALYTICAL PHASE

The objective of the analytical phase was to determine the residue levels of clopyralid in samples harvested during the field phase.

#### Experimental details

##### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trial.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table::

#### TRIAL No. C2132 PL1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2132 01 01	C2132 PL1 / U1 / A	18/05/2022	08/02/2023	266	11/02/2023	3
C2132 01 02	C2132 PL1 / T1 / A	18/05/2022	08/02/2023	266	16/02/2023	8
C2132 01 03	C2132 PL1 / T2 / A	24/05/2022	08/02/2023	260	16/02/2023	8
C2132 01 04	C2132 PL1 / T3 / A	10/06/2022	08/02/2023	243	16/02/2023	8
C2132 01 05	C2132 PL1 / T4R / A	27/06/2022	14/02/2023	232	18/02/2023	4
C2132 01 06	C2132 PL1 / T4L / A	27/06/2022	10/02/2023	228	16/02/2023	6
C2132 01 07	C2132 PL1 / UHR / A	16/09/2022	14/02/2023	151	17/02/2023	3
C2132 01 08	C2132 PL1 / UHL / A	16/09/2022	10/02/2023	147	11/02/2023	1
C2132 01 09	C2132 PL1 / THR / A	16/09/2022	14/02/2023	151	17/02/2023	3
C2132 01 10	C2132 PL1 / THL / A	16/09/2022	10/02/2023	147	11/02/2023	1

#### Storage stability of specimens

Specimens were stored frozen for no more than 266 days from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in commodities with high water, high oil, high acid and dry/high starch content (EFSA Journal Volume19, Issue1, January 2021, e06389).

#### Storage stability of extracts

After extraction, samples were stored refrigerated and analysed after maximum 8 days.

Results of storage stability of extracts in ANADIAG validation study No. C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities” showed a good stability of clopyralid residues for up to 15 days of refrigerated storage for high water content.

#### Specimen preparation

The specimens were prepared according to ANADIAG SOPs.

The sample was blended with dry ice and placed for at least 12 hours at  $T < -18^{\circ}\text{C}$  for sublimation of dry ice. The amount required by the analytical method (2 g) was weighed from this homogeneous matrix.

#### Specimen analysis

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

Outline of ANADIAG method:

Residues of clopyralid and its conjugates are extracted and hydrolysed from samples by heating at  $60^{\circ}\text{C}$  for 3 hours with 2.5M KOH. After acidification with  $\text{H}_2\text{SO}_4$ , addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract is purified with a liquid-liquid partition. An aliquot of the upper layer is evaporated to dryness and the sample is reconstituted in 50:50, methanol/ $\text{H}_2\text{O}$  + 0.1% formic acid. Extracts are analysed by LC-MS/MS.

ANADIAG References (French version) of the method are

for the preparation and extraction of the samples: **SOP MP 718**

for the analysis of extracts and for the calibration: **SOP MA 1809**

#### LOD

The limit of detection (LOD) was expressed as lowest calibration standard.

The LOD was 0.4 ng/mL for clopyralid in high water content (corresponding to 0.002 mg/kg for clopyralid and 0.003 mg/kg for clopyralid glycine).

#### LOQ

## The LOQ was 0.01 mg/kg for clopyralid and clopyralid glycine in high water content.

### Preparation of standard solutions

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

	Solvent	Concentration	Storage conditions	Expiry date (Preparation + ...)
<b>Stock solution Clopyralid</b>	Acetonitrile	≈ 1 mg/mL	Frozen	6 months
<b>Stock solution Clopyralid glycine</b>	Methanol	≈ 1 mg/mL	Frozen	6 months
<b>Spiking solutions All analyte separately</b>	Acetonitrile	≈ 0.2, 2 and 20 µg/mL	Frozen	1 month
<b>Intermediate calibration solutions Clopyralid<sup>(1)</sup></b>	Control extract	≈ 200 and 20 ng/mL	Refrigerated	14 days
<b>Matrix-matched Calibration solutions Clopyralid<sup>(1)</sup></b>	Control extract	≈ 0.4 to 24 ng/mL	Refrigerated	14 days
<b>Intermediate calibration solutions Clopyralid<sup>(2)</sup></b>	Methanol / water (50/50) + 0.1% formic acid	≈ 200 and 20 ng/mL	Refrigerated	14 days
<b>Calibration solution Clopyralid<sup>(2)</sup></b>	Methanol / water (50/50) + 0.1% formic acid	≈ 0.4 to 24 ng/mL	Refrigerated	14 days

<sup>(1)</sup> For analysis of undiluted extracts

<sup>(2)</sup> For analysis of diluted extracts (dilution factor ≥ 20)

### Calibration curves

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas of clopyralid obtained from chromatograms were plotted versus concentration and the calibration functions were determined by least square fit.

Number and concentrations of standards used, as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve (r) should be ≥ 0.990 for the calibration to be acceptable with regression residuals randomly distributed.

All extracts analysed (after dilution when required) fell within the range of the standard curve.

### Fortification procedure

Fortifications were performed by adding known amounts of the spiking solutions to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

The spiked samples for roots and leaves with tops were done on untreated samples available at ANADIAG laboratory (ANADIAG sample No. S593 for whole plants, S595 for roots and S594 for leaves with tops). The absence of the analyte in these samples was checked within this study. The amount found was not detectable

Analytical Sample No.	Matrix	Fortification level (mg/kg)	Clopyralid % Recovery	Clopyralid glycine % Recovery	Extraction date
S593 01 AA	Whole plants	0.01	81.3%	-	07/02/2023
S593 01 BA	Whole plants	0.10	98.1%	-	08/02/2023
S593 01 CA	Whole plants	0.01	-	71.3%	08/02/2023
S593 01 DA	Whole plants	0.10	-	77.8%	07/02/2023
S593 01 EA d250	Whole plants	25	107.2%	-	15/02/2023
S593 01 FA d250	Whole plants	25	-	100.7%	15/02/2023
S594 01 AA	Leaves with tops	0.01	92.8%	-	09/02/2023
S594 01 BA	Leaves with tops	0.10	91.9%	-	10/02/2023
S594 01 CA	Leaves with tops	0.01	-	71.9%	10/02/2023
S594 01 DA	Leaves with tops	0.10	-	74.2%	09/02/2023
S594 01 EA d10	Leaves with tops	1.0	96.5%	-	15/02/2023
S594 01 FA d10	Leaves with tops	1.0	-	83.9%	15/02/2023
S595 01 AA	Roots	0.01	99.8%	-	13/02/2023
S595 01 BA	Roots	0.10	95.7%	-	14/02/2023
S595 01 CA	Roots	0.01	-	72.4%	14/02/2023
S595 01 DA	Roots	0.10	-	79.7%	13/02/2023
S595 01 EA D10	Roots	1.0	102.1%	-	17/02/2023
S595 01 FA D10	Roots	1.0	-	76.1%	17/02/2023

The recoveries of the spiked samples met with the acceptance criteria described in SANTE/2020/12830, Rev.1.

## Results

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2132 PL1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2132 01 01	C2132 PL1 / U1 / A	-	Whole plants	-	NDR
C2132 01 02	C2132 PL1 / T1 / A	CHR/H/CPD 300 SL	Whole plants	0	13.36
C2132 01 03	C2132 PL1 / T2 / A	CHR/H/CPD 300 SL	Whole plants	6	0.97
C2132 01 04	C2132 PL1 / T3 / A	CHR/H/CPD 300 SL	Whole plants	23	0.97
C2132 01 05	C2132 PL1 / T4R / A	CHR/H/CPD 300 SL	Roots	40	0.29
C2132 01 06	C2132 PL1 / T4L / A	CHR/H/CPD 300 SL	Leaves with tops	40	0.27
C2132 01 07	C2132 PL1 / UHR / A	-	Roots	-	NDR
C2132 01 08	C2132 PL1 / UHL / A	-	Leaves with tops	-	NDR
C2132 01 09	C2132 PL1 / THR / A	CHR/H/CPD 300 SL	Roots	121	0.05
C2132 01 10	C2132 PL1 / THL / A	CHR/H/CPD 300 SL	Leaves with tops	121	0.07

DAA: Days After Application

NDR: No detectable residues (residues below the limit of detection)

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

### A 2.1.3.1.1.8 Study 8

Reference: KCA 6.3/08

<b>Report</b>	Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Sugar Beets Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022, M. Lefebvre 2023, C2133, Anadiag, France
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<b>Guideline(s):</b>	Regulation (EC) No. 1107/2009 Regulation (EU) No. 283/2013 and 284/2013 2004/10/EC GLP Directive OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021 SANTE/2019/12752 - Technical guidelines on data requirements for setting Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin. SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.
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<b>Deviations:</b>	No
<b>GLP:</b>	Yes
<b>Acceptability:</b>	Yes

### Objective of the study

The objective of the study was to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Sugar beet raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.5 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at 1 site in Northern Europe. The trial was sampled at harvest.

One plot was treated once with CHR/H/CPD 300 SL at BBCH 14, at the application rate of 0.5 L/ha (150 g clopyralid/ha).

One plot remained untreated.

Sampling was performed at normal commercial harvest (BBCH 49) in treated and untreated plots.

Clopyralid (Sum of clopyralid, its salts and conjugates) residues were analysed in samples harvested during the field phase.

### Field phase description

The objective of the study was to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Sugar beet raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.5 L/ha.

The following pattern was designed for the treatments and the samplings:

#### 1.1.1.1 Application details

Plot	Test Item	App. No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	CHR/H/CPD 300 SL	T1	BBCH 14	0.5 L/ha	150 g/ha	200-300 L/ha (±10%)

### 1.1.1.2 Sampling Details

#### Residue at harvest trial :

Sampling event	Plot	Timing	Matrix	Min. Sample size
S1	U, T	NCH BBCH 49	Roots	2 kg, from min. 12 plants
			Leaves with tops	1 kg, from min. 12 plants

NCH: Normal Commercial harvest

#### Location of the trial

The trial was performed on soil type and under cultural practices typical for sugar beet production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Type of trial	Crop	European area	Region, Country
1	C2133 PL1	Krzysztof NOWAK	RH	Sugar beet	North	Łódzkie, Poland

RH: Residue at harvest



#### Identity and composition of the test item(s):

##### Test item

Trade or Code Name	CHR/H/CPD 300 SL
Active substance (a.s.)	Clopyralid
Formulation type	SL
CAS Number	[1702-17-6]



<b>Nominal content of a.s.</b>	300 g/L (expressed as clopyralid)
<b>Batch number*</b>	02/2018
<b>Actual content *</b>	30.18 %
<b>Expiry date*</b>	31/12/2022

## General Information on the trial

### Crop and soil Information

Trial No.	Crop	Variety	Crop density	Sowing / Planting date	Soil type	pH	Organic matter (%)
C2133 PL1	Sugar beet	Valzer	11.11 seeds/m <sup>2</sup>	31/03/2022	Sandy clay loam	6.5	2.0

### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (m)	Pressure (bars)
C2133 PL1	EUROPULVE	Flat fan	Teejet XR 110 02 VS	3.0	9	0.33	3.0

### Summary of the actual application(s) data

Trial No.	Plot	Application No.	Active substance rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2133 PL1	T	1	153.3	+2.2	307	17/05/2022	14

### Sampling of specimens

Trial No	Sampling	Actual Date	Actual timing	Actual Growth Stage (BBCH)
C2133 PL1	1	06/10/2022	NCH, 142 DAA	49

DAA: Days after application

NCH: Normal commercial harvest

## ANALYTICAL PHASE

The objective of the analytical phase was to determine the residue levels of clopyralid in samples harvested during the field phase.

### Experimental details

#### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trial.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table::

#### TRIAL No. C2133 PL1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2133 01 01	C2133 PL1 / UHR / A	06/10/2022	17/02/2023	134	18/02/2023	1
C2133 01 02	C2133 PL1 / UHL / A	06/10/2022	20/02/2023	137	21/02/2023	1
C2133 01 03	C2133 PL1 / THR / A	06/10/2022	17/02/2023	134	18/02/2023	1
C2133 01 04	C2133 PL1 / THL / A	06/10/2022	20/02/2023	137	21/02/2023	1

\*Frozen storage time of samples from sampling to extraction (days)

\*\*Refrigerated storage time of final extracts, from extraction to analysis (days)

#### Storage stability of specimens

Specimens were stored frozen for no more than 137 days from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in commodities with high water, high oil, high acid and dry/high starch content (EFSA Journal Volume19, Issue1, January 2021, e06389).

#### Storage stability of extracts

After extraction, samples were stored refrigerated and analysed after maximum 1 day.

Results of storage stability of extracts in ANADIAG validation study No. C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities” showed a good stability of clopyralid residues for up to 15 days of refrigerated storage for high water content.

#### Specimen preparation

The specimens were prepared according to ANADIAG SOPs.

The sample was blended with dry ice and placed for at least 12 hours at  $T < -18^{\circ}\text{C}$  for sublimation of dry ice. The amount required by the analytical method (2 g) was weighed from this homogeneous matrix.

#### Specimen analysis

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

Outline of ANADIAG method:

Residues of clopyralid and its conjugates are extracted and hydrolysed from samples by heating at  $60^{\circ}\text{C}$  for 3 hours with 2.5M KOH. After acidification with  $\text{H}_2\text{SO}_4$ , addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract is purified with a liquid-liquid partition. An aliquot of the upper layer is evaporated to dryness and the sample is reconstituted in 50:50, methanol/ $\text{H}_2\text{O}$  + 0.1% formic acid. Extracts are analysed by LC-MS/MS.

ANADIAG References (French version) of the method are

for the preparation and extraction of the samples: **SOP MP 718**

for the analysis of extracts and for the calibration: **SOP MA 1809**

#### LOD

The limit of detection (LOD) was expressed as lowest calibration standard.

The LOD was 0.4 ng/mL for clopyralid in high water content (corresponding to 0.002 mg/kg for clopyralid and 0.003 mg/kg for clopyralid glycine).

#### LOQ

The LOQ was 0.01 mg/kg for clopyralid and clopyralid glycine in high water content.

Preparation of standard solutions

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commer-



## cial reference item.

	Solvent	Concentration	Storage conditions	Expiry date (Preparation + ...)
<b>Stock solution Clopyralid</b>	Acetonitrile	≈ 1 mg/mL	Frozen	6 months
<b>Stock solution Clopyralid glycine</b>	Methanol	≈ 1 mg/mL	Frozen	6 months
<b>Spiking solutions All analyte separately</b>	Acetonitrile	≈ 0.2 and 2 µg/mL	Frozen	1 month
<b>Intermediate calibration solutions Clopyralid</b>	Control extract	≈ 200 and 20 ng/mL	Refrigerated	14 days
<b>Matrix-matched Calibration solutions Clopyralid</b>	Control extract	≈ 0.4 to 24 ng/mL	Refrigerated	14 days

## Calibration curves

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas of clopyralid obtained from chromatograms were plotted versus concentration and the calibration functions were determined by least square fit.

Number and concentrations of standards used, as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve ( $r$ ) should be  $\geq 0.990$  for the calibration to be acceptable with regression residuals randomly distributed.

All extracts analysed (after dilution when required) fell within the range of the standard curve.

## Fortification procedure

Fortifications were performed by adding known amounts of the spiking solutions to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

The spiked samples for roots and leaves with tops were done on untreated samples available at ANADIAG laboratory (ANADIAG sample No. S597 and S595 for roots and S598 for leaves with tops). The absence of the analyte in these samples was checked within this study. The amount found was not detectable

Analytical Sample No.	Matrix	Fortification level (mg/kg)	Clopyralid % Recovery	Clopyralid glycine % Recovery	Extraction date
S597 01 AA	Roots	0.01	111.2%	-	17/02/2023
S597 01 BA	Roots	0.10	108.6%	-	17/02/2023
S595 01 EA D10	Roots	1.0	102.1%	-	17/02/2023
S597 01 CA	Roots	0.01	-	86.1%	17/02/2023
S597 01 DA	Roots	0.10	-	79.8%	17/02/2023
S595 01 FA D10	Roots	1.0	-	76.1%	17/02/2023
S598 01 AA	Leaves with tops	0.01	115.6%	-	20/02/2023
S598 01 BA D10	Leaves with tops	1.0	91.7%	-	20/02/2023
S598 01 CA	Leaves with tops	0.01	-	78.9%	20/02/2023
S598 01 DA D10	Leaves with tops	1.0	-	94.6%	20/02/2023

The recoveries of the spiked samples met with the acceptance criteria described in SANTE/2020/12830, Rev.1.

## Results

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2133 PL1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2133 01 01	C2133 PL1 / UHR / A	-	Roots	-	NDR
C2133 01 02	C2133 PL1 / UHL / A	-	Leaves with tops	-	NDR
C2133 01 03	C2133 PL1 / THR / A	CHR/H/CPD 300 SL	Roots	142	0.04
C2133 01 04	C2133 PL1 / THL / A	CHR/H/CPD 300 SL	Leaves with tops	142	0.06

DAA: Days After Application

NDR: No detectable residues (residues below the limit of detection)

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

### A 2.1.3.1.1.9 Study 9

Reference:	KCA 6.3/09
Report	Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Sugar Beets Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022, M. Lefebvre 2023, C2134, Anadiag, France
Guideline(s):	Regulation (EC) No. 1107/2009 Regulation (EU) No. 283/2013 and 284/2013 2004/10/EC GLP Directive OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021 SANTE/2019/12752 - Technical guidelines on data requirements for setting Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin.

SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes  
OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.

Deviations:	No
GLP:	Yes
Acceptability:	Yes

### Objective of the study

The objective of the study was to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Sugar beet raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.5 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at 1 site in Northern Europe. The trial was sampled at harvest.

One plot was treated once with CHR/H/CPD 300 SL at BBCH 14, at the application rate of 0.5 L/ha (150 g clopyralid/ha).

One plot remained untreated.

Sampling was performed at normal commercial harvest (BBCH 49) in treated and untreated plots.

Clopyralid (Sum of clopyralid, its salts and conjugates) residues were analysed in samples harvested during the field phase..

### Field phase description

The objective of the study was to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Sugar beet raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.5 L/ha.

The following pattern was designed for the treatments and the samplings:

#### 1.1.1.1 Application details

Plot	Test Item	App. No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	CHR/H/CPD 300 SL	T1	BBCH 14	0.5 L/ha	150 g/ha	200-300 L/ha (±10%)

#### 1.1.1.2 Sampling Details

##### Residue at harvest trial :

Sampling event	Plot	Timing	Matrix	Min. Sample size
S1	U, T	NCH BBCH 49	Roots	2 kg, from min. 12 plants
			Leaves with tops	1 kg, from min. 12 plants

NCH: Normal Commercial harvest

### Location of the trial

The trial was performed on soil type and under cultural practices typical for sugar beet production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Type of trial	Crop	European area	Region, Country
1	C2134 CZ1	Iva SIMEK	RH	Sugar beet	North	Hradec Králové, Czech Republic

RH: Residue at harvest



#### Identity and composition of the test item(s):

##### Test item

Trade or Code Name	CHR/H/CPD 300 SL
Active substance (a.s.)	Clopyralid
Formulation type	SL
CAS Number	[1702-17-6]
Nominal content of a.s.	300 g/L (expressed as clopyralid)
Batch number*	02/2018
Actual content *	30.18 %
Expiry date*	31/12/2022

#### General Information on the trial

##### Crop and soil Information

Trial No.	Crop	Variety	Crop density (plants/ha)	Sowing / Planting date	Soil type	pH	Organic matter (%)
C2134 CZ1	Sugar beet	Kaplan	100 000	29/03/2022	Loam	6.1	2.2

##### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (m)	Pressure (bars)
C2134 CZ1	PULVEXPER	Flat fan	Teejet XR 110 015 VS	3	9	0.33	2

#### Summary of the actual application(s) data

Trial No.	Plot	Application No.	Active substance rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2134 CZ1	T	1	142.9	-4.8	238	10/05/2022	14

#### Sampling of specimens

Trial No	Sampling	Actual Date	Actual timing	Actual Growth Stage (BBCH)
C2134 CZ1	1	26/09/2022	NCH, 139 DAA	49

DAA: Days after application

NCH: Normal commercial harvest

#### ANALYTICAL PHASE

The objective of the analytical phase was to determine the residue levels of clopyralid in samples harvested during the field phase.

#### Experimental details

##### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trial.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table::

##### TRIAL No. C2134 CZ1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2134 01 01	C2134 CZ1 / UHR / A	26/09/2022	17/02/2023	144	18/02/2023	1
C2134 01 02	C2134 CZ1 / UHL / A	26/09/2022	20/02/2023	147	21/02/2023	1
C2134 01 03	C2134 CZ1 / THR / A	26/09/2022	17/02/2023	144	18/02/2023	1
C2134 01 04	C2134 CZ1 / THL / A	26/09/2022	20/02/2023	147	21/02/2023	1

\*Frozen storage time of samples from sampling to extraction (days)

\*\*Refrigerated storage time of final extracts, from extraction to analysis (days)

#### Storage stability of specimens

Specimens were stored frozen for no more than 147 days from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in commodities with high water, high oil, high acid and dry/high starch content (EFSA Journal Volume19, Issue1, January 2021, e06389).

### Storage stability of extracts

After extraction, samples were stored refrigerated and analysed after maximum 1 day.

Results of storage stability of extracts in ANADIAG validation study No. C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities” showed a good stability of clopyralid residues for up to 15 days of refrigerated storage for high water content.

### Specimen preparation

The specimens were prepared according to ANADIAG SOPs.

The sample was blended with dry ice and placed for at least 12 hours at  $T < -18^{\circ}\text{C}$  for sublimation of dry ice. The amount required by the analytical method (2 g) was weighed from this homogeneous matrix.

### Specimen analysis

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

Outline of ANADIAG method:

Residues of clopyralid and its conjugates are extracted and hydrolysed from samples by heating at  $60^{\circ}\text{C}$  for 3 hours with 2.5M KOH. After acidification with  $\text{H}_2\text{SO}_4$ , addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract is purified with a liquid-liquid partition. An aliquot of the upper layer is evaporated to dryness and the sample is reconstituted in 50:50, methanol/ $\text{H}_2\text{O}$  + 0.1% formic acid. Extracts are analysed by LC-MS/MS.

ANADIAG References (French version) of the method are

for the preparation and extraction of the samples: **SOP MP 718**

for the analysis of extracts and for the calibration: **SOP MA 1809**

### LOD

The limit of detection (LOD) was expressed as lowest calibration standard.

The LOD was 0.4 ng/mL for clopyralid in high water content (corresponding to 0.002 mg/kg for clopyralid and 0.003 mg/kg for clopyralid glycine).

### LOQ

The LOQ was 0.01 mg/kg for clopyralid and clopyralid glycine in high water content.

### Preparation of standard solutions

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

	Solvent	Concentration	Storage conditions	Expiry date (Preparation + ...)
Stock solution Clopyralid	Acetonitrile	$\approx 1 \text{ mg/mL}$	Frozen	6 months
Stock solution Clopyralid glycine	Methanol	$\approx 1 \text{ mg/mL}$	Frozen	6 months
Spiking solutions All analyte separately	Acetonitrile	$\approx 0.2$ and $2 \text{ }\mu\text{g/mL}$	Frozen	1 month
Intermediate calibration solutions Clopyralid	Control extract	$\approx 200$ and $20 \text{ ng/mL}$	Refrigerated	14 days
Matrix-matched Calibration solutions Clopyralid	Control extract	$\approx 0.4$ to $24 \text{ ng/mL}$	Refrigerated	14 days

### Calibration curves

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as



the specimens.

Peak areas of clopyralid obtained from chromatograms were plotted versus concentration and the calibration functions were determined by least square fit.

Number and concentrations of standards used, as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve (r) should be  $\geq 0.990$  for the calibration to be acceptable with regression residuals randomly distributed.

All extracts analysed (after dilution when required) fell within the range of the standard curve.

### Fortification procedure

Fortifications were performed by adding known amounts of the spiking solutions to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

The spiked samples for roots and leaves with tops were done on untreated samples available at ANADIAG laboratory (ANADIAG sample No. S597 and S595 for roots and S598 for leaves with tops). The absence of the analyte in these samples was checked within this study. The amount found was not detectable.

Analytical Sample No.	Matrix	Fortification level (mg/kg)	Clopyralid % Recovery	Clopyralid glycine % Recovery	Extraction date
S597 01 AA	Roots	0.01	111.2%	-	17/02/2023
S597 01 BA	Roots	0.10	108.6%	-	17/02/2023
S595 01 EA D10	Roots	1.0	102.1%	-	17/02/2023
S597 01 CA	Roots	0.01	-	86.1%	17/02/2023
S597 01 DA	Roots	0.10	-	79.8%	17/02/2023
S595 01 FA D10	Roots	1.0	-	76.1%	17/02/2023
S598 01 AA	Leaves with tops	0.01	115.6%	-	20/02/2023
S598 01 BA D10	Leaves with tops	1.0	91.7%	-	20/02/2023
S598 01 CA	Leaves with tops	0.01	-	78.9%	20/02/2023
S598 01 DA D10	Leaves with tops	1.0	-	94.6%	20/02/2023

The recoveries of the spiked samples met with the acceptance criteria described in SANTE/2020/12830, Rev.1.

### Results

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2134 CZ1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2134 01 01	C2134 CZ1 / UHR / A	-	Roots	-	NDR
C2134 01 02	C2134 CZ1 / UHL / A	-	Leaves with tops	-	NDR
C2134 01 03	C2134 CZ1 / THR / A	CHR/H/CPD 300 SL	Roots	139	0.04
C2134 01 04	C2134 CZ1 / THL / A	CHR/H/CPD 300 SL	Leaves with tops	139	0.06

DAA: Days After Application

NDR: No detectable residues (residues below the limit of detection)

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

March 2024

### Oil seed rape

The objective of the studies were to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in oil seed rape raw agricultural commodity (RAC) after one foliar application (at BBCH 51) of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha. Eight independent trials (Czech Republic, Germany, Poland and Netherland) are accepted and valid in relation to storage stability data. Residues are below MRL established for oil seed rape (Reg. (EU) 2021/1807).

Note: The maps presented in the studies do not contain the correct locations of the studies.

#### A 2.1.3.1.1.10 Study 10

Reference:	KCA 6.3/10
Report	Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Oilseed Rape Following One Foliar application with Faworyt 300 SL under Field Conditions in Northern Europe in 2022, E. Thomas-Delille, 2023, C2104, Anadiag, France
Guideline(s):	Regulation (EC) No. 1107/2009 Regulation (EU) No. 283/2013 and 284/2013 2004/10/EC GLP Directive OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021 SANTE/2019/12752 - Technical guidelines on data requirements for setting Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin. SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.
Deviations:	Deviation No. 28/11/2022 During the shipment, the temperature was above -18°C for 10h10 at total on 23-24/11/2022 with a maximum at -7.5 °C on 24/11/2022. The temperature was between -13°C and -5°C for 7h15 instead of a maximum duration of 3h allowed by the study plan. The following samples were concerned by this deviation: C2104 CZ1/UH/R and C2104 CZ1/TH/R. The deviation was due to a technical issue with the freezer truck during connection to the electrical network overnight at a test site. This deviation has no impact on the study as the analytical samples were shipped in good conditions and the spare specimens were not analysed.
GLP:	Yes
Acceptability:	Yes

#### Objective of the study

The objective of the study was to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Oilseed rape raw agricultural commodity (RAC) after one foliar application of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha..

The study consisted of two phases: the field phase and the analytical phase.



The study was conducted under field conditions at 1 site in Northern Europe. The trial was sampled frequently to monitor the decline of residues shortly after the treatment.

One plot was treated once with FAWORYT 300 SL at BBCH 51, at the application rate of 0.4 L/ha (120 g clopyralid/ha).

One plot remained untreated.

Sampling was performed at 0 DBA on untreated plot and 0 DAA on the treated plot, then treated plot was sampled at BBCH 59, BBCH 69 and at BBCH 79. At BBCH 89 (at maturity of the crop) untreated and treated plots were sampled.

Clopyralid (Sum of clopyralid, its salts and conjugates) residues were analysed in samples harvested during the field phase..

### Field phase description

The objective of the study was to determine the residue levels of Clopyralid (Sum of clopyralid, its salts and conjugates) in Oilseed rape raw agricultural commodity (RAC) after one foliar application of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The following pattern was designed for the treatments and the samplings:

#### 1.1.1.1 Application details

Plot	Test Item	App. No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	<b>FAWORYT 300 SL</b>	T1	BBCH 51	0.4 L/ha	120 g/ha	200-300 L/ha (±10%)

#### 1.1.1.2 Sampling Details

##### Decline curve trial

Sampling event	Plot	Timing	Matrix	Min. Sample size
<b>S1</b>	U	<b>0 DBA</b>	Whole plants	0.5 kg
	T	<b>0 DAA</b>	Whole plants	0.5 kg
<b>S2</b>	T	BBCH 59	Whole plants	0.5 kg
<b>S3</b>	T	BBCH 69	Whole plants	0.5 kg
<b>S4</b>	T	BBCH 79	Whole plants	1kg
<b>S5</b>	U, T	BBCH 89 (NCH)	Seeds	<b>2 kg</b>

DBA : Days Before Application

DAA : Days After Application

NCH: Normal Commercial Harvest

### Location of the trial

The trial was performed on soil type and under cultural practices typical for oilseed rape production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Type of trial	Crop	European area	Region Country
<b>1</b>	<b>C2104 CZ1</b>	Iva SIMEK	DC	Oilseed Rape	North	Pardubice, Czech Republic

DC: Decline curve

## Location



1 Trial C2104 CZ1

## Identity and composition of the test item(s):

### Test item

Trade or Code Name	FAWORYT 300 SL
Active substance (a.s.)	Clopyralid
Formulation type	SL
CAS Number	[1702-17-6]
Nominal content of a.s.	300 g/L (expressed as clopyralid)
Batch number*	202203001
Actual content *	302.2 g/L (expressed as clopyralid)
Expiry date*	11/03/2025

## General Information on the trial

### Crop and soil Information

Trial No.	Crop	Variety	Crop density (kg/ha)	Sowing / Planting date	Soil type	pH	Organic matter (%)
C2104 CZ1	Oilseed Rape	ARABELLA LG	3.5	18/08/2021	Clay Sandy Loam	5.3	2.0

### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (m)	Pressure (bars)
<b>C2104 CZ1</b>	PULVEXPER	Flat fan	Teejet XR 110 015 VS	3	9	0.33	2

#### Summary of the actual application(s) data

Trial No.	Plot	Application No.	a.s. rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
<b>C2104 CZ1</b>	T	1	122.7	+2.2	256	20/04/2022	51

a.s.: active substance

#### Sampling of specimens

Trial No	Sampling	Actual Date	Actual DAA	Actual Growth Stage (BBCH)
<b>C2104 CZ1</b>	1	20/04/2022	0 DBA / 0 DAA	51
	2	26/04/2022	6	59
	3	22/05/2022	32	69
	4	16/06/2022	57	79
	5	12/07/2022	83	89

DAA: Days After Application

DBA: Days Before Application

#### ANALYTICAL PHASE

The objective of the analytical phase was to determine the residue levels of clopyralid in samples harvested during the field phase.

#### Experimental details

##### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trial.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table::

#### TRIAL No. C2104 CZ1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2104 01 01	C2104 CZ1 / U0 / A	20/04/2022	02/02/2023	288	04/02/2023	2
C2104 01 02	C2104 CZ1 / T0 / A	20/04/2022	02/02/2023	288	05/02/2023	3
C2104 01 03	C2104 CZ1 / T59 / A	26/04/2022	02/02/2023	282	05/02/2023	3
C2104 01 04	C2104 CZ1 / T69 / A	22/05/2022	02/02/2023	256	05/02/2023	3
C2104 01 05	C2104 CZ1 / T79 / A	16/06/2022	02/02/2023	231	05/02/2023	3
C2104 01 06	C2104 CZ1 / UH / A	12/07/2022	26/01/2023	198	04/02/2023	9
C2104 01 07	C2104 CZ1 / TH / A	12/07/2022	26/01/2023	198	04/02/2023	9

\*Frozen storage time of samples from sampling to extraction (days)

\*\*Refrigerated storage time of final extracts, from extraction to analysis (days)

#### Storage stability of specimens

Specimens were stored frozen for no more than 288 days from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in commodities with high water, high oil, high acid and dry/high starch content (EFSA Journal Volume19, Issue1, January 2021, e06389).

#### Storage stability of extracts

After extraction, samples were stored refrigerated and analysed after maximum 3 days for whole plant and 9 days for seeds.

Results of storage stability of extracts in ANADIAG validation study No. C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities” showed a good stability of clopyralid residues for up to 15 days of refrigerated storage for high water content and 19 days of refrigerated storage for high oil content.

#### Specimen preparation

The specimens were prepared according to ANADIAG SOPs.

The sample was blended with dry ice and placed for at least 12 hours at  $T < -18^{\circ}\text{C}$  for sublimation of dry ice. The amount required by the analytical method (2 g) was weighed from this homogeneous matrix.

#### Specimen analysis

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

Outline of ANADIAG method:

Residues of clopyralid and its conjugates are extracted and hydrolysed from samples by heating at  $60^{\circ}\text{C}$  for 3 hours with 2.5M KOH. After acidification with  $\text{H}_2\text{SO}_4$ , addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract is purified with a liquid-liquid partition. An aliquot of the upper layer is evaporated to dryness and the sample is reconstituted in 50:50, methanol/ $\text{H}_2\text{O}$  + 0.1% formic acid. Extracts are analysed by LC-MS/MS.

ANADIAG References (French version) of the method are

for the preparation and extraction of the samples: **SOP MP 718**

for the analysis of extracts and for the calibration: **SOP MA 1809**

#### LOD

The limit of detection (LOD) was expressed as lowest calibration standard.

The LOD was 0.4 ng/mL for clopyralid in high water content (corresponding to 0.002 mg/kg for clopyralid and 0.003 mg/kg for clopyralid glycine).

#### LOQ

## The LOQ was 0.01 mg/kg for clopyralid and clopyralid glycine in high water content.

### Preparation of standard solutions

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

	Solvent	Concentration	Storage conditions	Expiry date (Preparation + ...)
Stock solution Clopyralid	Acetonitrile	≈ 1 mg/mL	Frozen	6 months
Stock solution Clopyralid glycine	Methanol	≈ 1 mg/mL	Frozen	6 months
Spiking solutions All analyte separately	Acetonitrile	≈ 0.2 and 2 µg/mL	Frozen	1 month
Intermediate calibration solutions Clopyralid <sup>(1)</sup>	Control extract	≈ 200 and 20 ng/mL	Refrigerated	14 days
Matrix-matched Calibration solutions Clopyralid <sup>(1)</sup>	Control extract	≈ 0.4 to 24 ng/mL	Refrigerated	14 days
Intermediate calibration solutions Clopyralid <sup>(2)</sup>	Methanol / water (50/50) + 0.1% formic acid	≈ 200 and 20 ng/mL	Refrigerated	14 days
Calibration solution Clopyralid <sup>(2)</sup>	Methanol / water (50/50) + 0.1% formic acid	≈ 0.4 to 24 ng/mL	Refrigerated	14 days

<sup>(1)</sup> For analysis of undiluted extracts

<sup>(2)</sup> For analysis of diluted extracts

### Calibration curves

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas of clopyralid obtained from chromatograms were plotted versus concentration and the calibration functions were determined by least square fit.

Number and concentrations of standards used, as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve (r) should be ≥ 0.990 for the calibration to be acceptable with regression residuals randomly distributed.

All extracts analysed (after dilution when required) fell within the range of the standard curve.

### Fortification procedure

Fortifications were performed by adding known amounts of the spiking solutions to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

The spiked samples for whole plant and seeds were done on untreated samples available at ANADIAG laboratory (ANADIAG sample No. S592 for whole plant and S587 for seeds). The absence of the analyte in these samples was checked within this study. The amount found was not detectable

The recoveries of the spiked samples met with the acceptance criteria described in SANTE/2020/12830, Rev.1.

Analytical Sample No.	Matrix	Fortification level (mg/kg)	Clopyralid % Recovery	Clopyralid glycine % Recovery	Extraction date
S592 01 AA	Whole plant	0.01	68.2%	-	02/02/2023
S592 01 BA	Whole plant	0.10	96.3%	-	03/02/2023
S592 01 CA	Whole plant	0.01	-	70.1%	03/02/2023
S592 01 DA	Whole plant	0.10	-	76.9%	02/02/2023
S592 01 EA D200	Whole plant	20	106.7%	-	02/02/2023
S592 01 FA D200	Whole plant	20	-	78.5%	02/02/2023
S587 01 AA	Seeds	0.01	75.6%	-	26/01/2023
S587 01 BA	Seeds	0.10	91.7%	-	27/01/2023
S587 01 CA	Seeds	0.01	-	61.5%	27/01/2023
S587 01 DA	Seeds	0.10	-	71.0%	26/01/2023

## Results

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2104 CZ1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2104 01 01	C2104 CZ1 / U0 / A	-	Whole plants	0	< LOQ
C2104 01 02	C2104 CZ1 / T0 / A	FAWORYT 300 SL	Whole plants	0	1.57
C2104 01 03	C2104 CZ1 / T59 / A	FAWORYT 300 SL	Whole plants	6	1.87
C2104 01 04	C2104 CZ1 / T69 / A	FAWORYT 300 SL	Whole plants	32	0.84
C2104 01 05	C2104 CZ1 / T79 / A	FAWORYT 300 SL	Whole plants	57	0.95
C2104 01 06	C2104 CZ1 / UH / A	-	Seeds	83	NDR
C2104 01 07	C2104 CZ1 / TH / A	FAWORYT 300 SL	Seeds	83	0.02

DAA: Days After Application

< LOQ: Residues between LOD and LOQ

NDR: No detectable residues (residues below the limit of detection)

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

### A 2.1.3.1.1.11 Study 11

Reference: KCA 6.3/11

Report: Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Oilseed Rape Following One Foliar application with Faworyt 300 SL under Field Conditions in Northern Europe in 2022, E. Thomas-Delille, 2023, C2120, Anadiag, France

Guideline(s): Regulation (EC) No. 1107/2009  
Regulation (EU) No. 283/2013 and 284/2013  
2004/10/EC GLP Directive  
OECD – guideline for the testing of chemicals, 509; Crop field trial,



14/06/2021

SANTE/2019/12752 - Technical guidelines on data requirements for setting Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin.

SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes

OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.

Deviations: No

GLP: Yes

Acceptability: Yes

### Objective of the study

The objective of the study was to determine the residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in Oilseed Rape raw agricultural commodity (RAC) after one foliar application of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at one site in Northern Europe. The trial was sampled frequently to monitor the decline of residues shortly after the treatment.

One plot was treated once with FAWORYT 300 SL at BBCH 51, at the application rate of 0.4 L/ha (120 g clopyralid/ha).

One plot remained untreated.

Samplings were performed at 0 DBA (day before application) on untreated plot and at 0 DAA (days after application) on the treated plot, then treated plot was sampled at BBCH 59, BBCH 69 and at BBCH 79.

At BBCH 89 (at maturity of the crop) untreated and treated plots were sampled.

Clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) residues were analysed in samples harvested during the field phase.

### Field phase description

The objective of the study was to determine the residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in Oilseed Rape raw agricultural commodity (RAC) after one foliar application of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The following pattern was designed for the treatments and the samplings:

#### 1.1.1.1 Application details

Plot	Test Item	App. No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	<b>FAWORYT 300 SL</b>	T1	BBCH 51	0.4 L/ha	120 g/ha	200-300 L/ha (±10%)

#### 1.1.1.2 Sampling Details

##### Decline curve trial

Sampling event	Plot	Timing	Matrix	Min. Sample size
<b>S1</b>	U	<b>0 DBA</b>	Whole plants	0.5 kg
	T	<b>0 DAA</b>	Whole plants	0.5 kg
<b>S2</b>	T	BBCH 59	Whole plants	0.5 kg
<b>S3</b>	T	BBCH 69	Whole plants	0.5 kg
<b>S4</b>	T	BBCH 79	Whole plants	1kg
<b>S5</b>	U, T	BBCH 89 (NCH)	Seeds	<b>2 kg</b>

DBA : Days Before Application  
DAA : Days After Application  
NCH: Normal Commercial Harvest

#### Location of the trial

The trial was performed on soil type and under cultural practices typical for oilseed rape production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Type of trial	Crop	European area	Region Country
<b>1</b>	<b>C2120 DE1</b>	Johannes SCHULZ	DC	Oilseed Rape	North	North Rhine-Westphalia, Germany

DC: Decline curve



## Location



## Identity and composition of the test item(s):

### Test item

<b>Trade or Code Name</b>	<b>FAWORYT 300 SL</b>
<b>Active substance (a.s.)</b>	Clopyralid
<b>Formulation type</b>	SL
<b>CAS Number</b>	[1702-17-6]
<b>Nominal content of a.s.</b>	300 g/L (expressed as clopyralid)
<b>Batch number*</b>	202203001
<b>Actual content *</b>	302.2 g/L (expressed as clopyralid)
<b>Expiry date*</b>	11/03/2025

## General Information on the trial

### Crop and soil Information

Trial No.	Crop	Variety	Crop density (seeds/m <sup>2</sup> )	Sowing / Planting date	Soil type	pH	Organic matter (%)
<b>C2120 DE1</b>	Oilseed Rape	ABILITY	120	05/04/2022	Sand	5.8	1.8

### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (m)	Pressure (bars)
<b>C2120 DE1</b>	BAUMANN	Flat fan	Lechler IDK 120-025 POM	3.0	6	0.50	3.0

### Summary of the actual application(s) data

Trial No.	Plot	Application No.	a.s. rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2120 DE1	T	1	124.0	+3.3	310	25/05/2022	51

a.s.: active substance

#### Sampling of specimens

Trial No	Sampling	Actual Date	Actual DAA	Actual Growth Stage (BBCH)
C2120 DE1	1	25/05/2022	0 DBA / 0 DAA	51
	2	29/05/2022	4	59
	3	25/06/2022	31	69
	4	04/08/2022	71	79
	5	22/08/2022	89	89

DAA: Days After Application

DBA: Days Before Application

### ANALYTICAL PHASE

The objective of the analytical phase was to determine the residue levels of clopyralid in samples harvested during the field phase.

#### Experimental details

##### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trial.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table::

#### TRIAL No. C2120 DE1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2120 01 01	C2120 DE1 / U0 / A	25/05/2022	02/02/2023	253	04/02/2023	2
C2120 01 02	C2120 DE1 / T0 / A	25/05/2022	02/02/2023	253	05/02/2023	3
C2120 01 03	C2120 DE1 / T59 / A	29/05/2022	02/02/2023	249	05/02/2023	3
C2120 01 04	C2120 DE1 / T69 / A	25/06/2022	02/02/2023	222	05/02/2023	3
C2120 01 05	C2120 DE1 / T79 / A	04/08/2022	02/02/2023	182	04/02/2023	2
C2120 01 06	C2120 DE1 / UH / A	22/08/2022	26/01/2023	157	04/02/2023	9
C2120 01 07	C2120 DE1 / TH / A	22/08/2022	26/01/2023	157	04/02/2023	9

\*Frozen storage time of samples from sampling to extraction (days)

\*\*Refrigerated storage time of final extracts, from extraction to analysis (days)

#### Storage stability of specimens

Specimens were stored frozen for no more than 253 days from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in commodities with high water, high oil, high acid and dry/high starch content (EFSA Journal Volume 19, Issue 1, January 2021, e06389).

#### **Storage stability of extracts**

After extraction, samples were stored refrigerated and analysed after maximum 3 days for whole plant and 9 days for seeds.

Results of storage stability of extracts in ANADIAG validation study No. C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities” showed a good stability of clopyralid residues for up to 15 days of refrigerated storage for high water content and 19 days of refrigerated storage for high oil content.

#### **Specimen preparation**

The specimens were prepared according to ANADIAG SOPs.

The sample was blended with dry ice and placed for at least 12 hours at  $T < -18^{\circ}\text{C}$  for sublimation of dry ice. The amount required by the analytical method (2 g) was weighed from this homogeneous matrix.

#### **Specimen analysis**

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

##### Outline of ANADIAG method:

Residues of clopyralid and its conjugates are extracted and hydrolysed from samples by heating at  $60^{\circ}\text{C}$  for 3 hours with 2.5M KOH. After acidification with  $\text{H}_2\text{SO}_4$ , addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract is purified with a liquid-liquid partition. An aliquot of the upper layer is evaporated to dryness and the sample is reconstituted in 50:50, methanol/ $\text{H}_2\text{O}$  + 0.1% formic acid. Extracts are analysed by LC-MS/MS.

ANADIAG References (French version) of the method are  
for the preparation and extraction of the samples:  
for the analysis of extracts and for the calibration:

**SOP MP 718**  
**SOP MA 1809**

#### **LOD**

**The limit of detection (LOD) was expressed as lowest calibration standard.**

**The LOD was 0.4 ng/mL for clopyralid in high water content (corresponding to 0.002 mg/kg for clopyralid and 0.003 mg/kg for clopyralid glycine).**

#### **LOQ**

**The LOQ was 0.01 mg/kg for clopyralid and clopyralid glycine in high water content.**

Preparation of standard solutions

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

Commercial reference item:				
	Solvent	Concentration	Storage conditions	Expiry date (Preparation + ...)
<b>Stock solution Clopyralid</b>	Acetonitrile	≈ 1 mg/mL	Frozen	6 months
<b>Stock solution Clopyralid glycine</b>	Methanol	≈ 1 mg/mL	Frozen	6 months
<b>Spiking solutions All analyte separately</b>	Acetonitrile	≈ 0.2 and 2 µg/mL	Frozen	1 month
<b>Intermediate calibration solutions Clopyralid<sup>(1)</sup></b>	Control extract	≈ 200 and 20 ng/mL	Refrigerated	14 days
<b>Matrix-matched Calibration solutions Clopyralid<sup>(1)</sup></b>	Control extract	≈ 0.4 to 24 ng/mL	Refrigerated	14 days
<b>Intermediate calibration solutions Clopyralid<sup>(2)</sup></b>	Methanol / water (50/50) + 0.1% formic acid	≈ 200 and 20 ng/mL	Refrigerated	14 days
<b>Calibration solution Clopyralid<sup>(2)</sup></b>	Methanol / water (50/50) + 0.1% formic acid	≈ 0.4 to 24 ng/mL	Refrigerated	14 days

(1) For analysis of undiluted extracts  
(2) For analysis of diluted extracts

### Calibration curves

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas of clopyralid obtained from chromatograms were plotted versus concentration and the calibration functions were determined by least square fit.

Number and concentrations of standards used, as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve ( $r$ ) should be  $\geq 0.990$  for the calibration to be acceptable with regression residuals randomly distributed.

All extracts analysed (after dilution when required) fell within the range of the standard curve.

### Fortification procedure

Fortifications were performed by adding known amounts of the spiking solutions to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

The spiked samples for whole plant and seeds were done on untreated samples available at ANADIAG laboratory (ANADIAG sample No. S592 for whole plant and S587 for seeds). The absence of the analyte in these samples was checked within this study. The amount found was not detectable

The recoveries of the spiked samples met with the acceptance criteria described in SANTE/2020/12830, Rev.1.

Analytical Sample No.	Matrix	Fortification level (mg/kg)	Clopyralid % Recovery	Clopyralid glycine % Recovery	Extraction date
S592 01 AA	Whole plant	0.01	68.2%	-	02/02/2023
S592 01 BA	Whole plant	0.10	96.3%	-	03/02/2023
S592 01 CA	Whole plant	0.01	-	70.1%	03/02/2023
S592 01 DA	Whole plant	0.10	-	76.9%	02/02/2023
S592 01 EA D200	Whole plant	20	106.7%	-	02/02/2023
S592 01 FA D200	Whole plant	20	-	78.5%	02/02/2023
S587 01 AA	Seeds	0.01	75.6%	-	26/01/2023
S587 01 BA	Seeds	0.10	91.7%	-	27/01/2023
S587 01 CA	Seeds	0.01	-	61.5%	27/01/2023
S587 01 DA	Seeds	0.10	-	71.0%	26/01/2023

## Results

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2120 DE1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2120 01 01	C2120 DE1 / U0 / A	-	Whole plants	-	NDR
C2120 01 02	C2120 DE1 / T0 / A	FAWORYT 300 SL	Whole plants	0	3.73
C2120 01 03	C2120 DE1 / T59 / A	FAWORYT 300 SL	Whole plants	4	1.10
C2120 01 04	C2120 DE1 / T69 / A	FAWORYT 300 SL	Whole plants	31	0.42
C2120 01 05	C2120 DE1 / T79 / A	FAWORYT 300 SL	Whole plants	71	NDR
C2120 01 06	C2120 DE1 / UH / A	-	Seeds	-	NDR
C2120 01 07	C2120 DE1 / TH / A	FAWORYT 300 SL	Seeds	89	NDR

DAA: Days After Application

NDR: No detectable residues (residues below the limit of detection)

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

### A 2.1.3.1.1.12 Study 12

Reference: KCA 6.3/12

Report: Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Oilseed Rape Following One Foliar application with Faworyt 300 SL under Field Conditions in Northern Europe in 2022, E. Thomas-Delille, 2023, C2121, Anadiag, France

Guideline(s): Regulation (EC) No. 1107/2009  
Regulation (EU) No. 283/2013 and 284/2013  
2004/10/EC GLP Directive  
OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021  
SANTE/2019/12752 - Technical guidelines on data requirements for setting

Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin.  
SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes  
OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.

Deviations:	No
GLP:	Yes
Acceptability:	Yes

### Objective of the study

The objective of the study was to determine the residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in Oilseed Rape raw agricultural commodity (RAC) after one foliar application of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at one site in Northern Europe. The trial was sampled at harvest.

One plot was treated once with FAWORYT 300 SL at BBCH 51, at the application rate of 0.4 L/ha (120 g clopyralid/ha).

One plot remained untreated.

Sampling was performed at BBCH 89 (at maturity of the crop) in untreated and treated plots.

Clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) residues were analysed in samples harvested during the field phase.

### Field phase description

The objective of the study was to determine the residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in Oilseed Rape raw agricultural commodity (RAC) after one foliar application of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The following pattern was designed for the treatments and the samplings:

#### 1.1.1.1 Application details

Plot	Test Item	App. No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	<b>FAWORYT 300 SL</b>	T1	BBCH 51	0.4 L/ha	120 g/ha	200-300 L/ha (±10%)

#### 1.1.1.2 Sampling Details

##### Residue at harvest

Sampling event	Plot	Timing	Matrix	Min. Sample size
S1	U, T	BBCH 89 (NCH)	Seeds	2 kg

NCH: Normal Commercial Harvest

### Location of the trial



The trial was performed on soil type and under cultural practices typical for oilseed rape production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Type of trial	Crop	European area	Region Country
1	C2121 BP1	Michael Elze	RH	Oilseed Rape	North	Opole, Poland

RH: Residue at Harvest

#### Location



#### Identity and composition of the test item(s):

##### Test item

Trade or Code Name	FAWORYT 300 SL
Active substance (a.s.)	Clopyralid
Formulation type	SL
CAS Number	[1702-17-6]
Nominal content of a.s.	300 g/L (expressed as clopyralid)
Batch number*	202203001
Actual content *	302.2 g/L (expressed as clopyralid)
Expiry date*	11/03/2025

#### General Information on the trial

##### Crop and soil Information

Trial No.	Crop	Variety	Crop density (seeds/m <sup>2</sup> )	Sowing / Planting date	Soil type	pH	Corg (%)
C2121 BP1	Oilseed Rape	INV 110 CL	100	22/04/2022	Sandy loam	5.9	1.1

##### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (m)	Pressure (bars)
C2121 BP1	AGROTOP	Flat fan	AIR MIX 110	2.5	10	0.25	2.5

#### Summary of the actual application(s) data

Trial No.	Plot	Application No.	a.s. rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2121 BP1	T	1	113.6	-5.3	284	01/06/2022	51

a.s.: active substance

#### Sampling of specimens

Trial No	Sampling	Actual Date	Actual DAA	Actual Growth Stage (BBCH)
C2121 BP1	1	09/08/2022	69	89

DAA: Days After Application

### ANALYTICAL PHASE

The objective of the analytical phase was to determine the residue levels of clopyralid in samples harvested during the field phase.

#### Experimental details

##### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trial.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table::

#### TRIAL No. C2121 BP1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2121 01 01	C2121 BP1 / UH / A	09/08/2022	26/01/2023	170	04/02/2023	9
C2121 01 02	C2121 BP1 / TH / A	09/08/2022	26/01/2023	170	04/02/2023	9

\*Frozen storage time of samples from sampling to extraction (days)

\*\*Refrigerated storage time of final extracts, from extraction to analysis (days)

#### Storage stability of specimens

Specimens were stored frozen for no more than 170 days from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in commodities with high water, high oil, high acid and dry/high starch content (EFSA Journal Volume19, Issue1, January 2021, e06389).

#### Storage stability of extracts

After extraction, samples were stored refrigerated and analysed after maximum 9 days for seeds.

Results of storage stability of extracts in ANADIAG validation study No. C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities” showed a good stability of clopyralid



residues for up to 19 days of refrigerated storage for high oil content.

### Specimen preparation

The specimens were prepared according to ANADIAG SOPs.

The sample was blended with dry ice and placed for at least 12 hours at  $T < -18^{\circ}\text{C}$  for sublimation of dry ice. The amount required by the analytical method (2 g) was weighed from this homogeneous matrix.

### Specimen analysis

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

#### Outline of ANADIAG method:

Residues of clopyralid and its conjugates are extracted and hydrolysed from samples by heating at  $60^{\circ}\text{C}$  for 3 hours with 2.5M KOH. After acidification with  $\text{H}_2\text{SO}_4$ , addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract is purified with a liquid-liquid partition. An aliquot of the upper layer is evaporated to dryness and the sample is reconstituted in 50:50, methanol/ $\text{H}_2\text{O}$  + 0.1% formic acid. Extracts are analysed by LC-MS/MS.

ANADIAG References (French version) of the method are

for the preparation and extraction of the samples:

**SOP MP 718**

for the analysis of extracts and for the calibration:

**SOP MA 1809**

### LOD

The limit of detection (LOD) was expressed as lowest calibration standard.

The LOD was 0.4 ng/mL for clopyralid in high water content (corresponding to 0.002 mg/kg for clopyralid and 0.003 mg/kg for clopyralid glycine).

### LOQ

The LOQ was 0.01 mg/kg for clopyralid and clopyralid glycine in high water content.

Preparation of standard solutions

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

	Solvent	Concentration	Storage conditions	Expiry date (Preparation + ...)
Stock solution Clopyralid	Acetonitrile	$\approx 1 \text{ mg/mL}$	Frozen	6 months
Stock solution Clopyralid glycine	Methanol	$\approx 1 \text{ mg/mL}$	Frozen	6 months
Spiking solutions All analyte separately	Acetonitrile	$\approx 0.2$ and $2 \text{ }\mu\text{g/mL}$	Frozen	1 month
Intermediate calibration solutions Clopyralid	Control extract	$\approx 200$ and $20 \text{ ng/mL}$	Refrigerated	14 days
Matrix-matched Calibration solutions Clopyralid	Control extract	$\approx 0.4$ to $24 \text{ ng/mL}$	Refrigerated	14 days

### Calibration curves

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas of clopyralid obtained from chromatograms were plotted versus concentration and the calibration functions were determined by least square fit.

Number and concentrations of standards used, as well as acceptability criteria are described in SOP No.

PG 0118. According to this SOP, the correlation coefficient for a curve (r) should be  $\geq 0.990$  for the calibration to be acceptable with regression residuals randomly distributed.  
All extracts analysed fell within the range of the standard curve.

### Fortification procedure

Fortifications were performed by adding known amounts of the spiking solutions to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

The spiked samples for whole plant and seeds were done on untreated samples available at ANADIAG laboratory (ANADIAG sample No. S592 for whole plant and S587 for seeds). The absence of the analyte in these samples was checked within this study. The amount found was not detectable

The recoveries of the spiked samples met with the acceptance criteria described in SANTE/2020/12830, Rev.1.

Analytical Sample No.	Matrix	Fortification level (mg/kg)	Clopyralid % Recovery	Clopyralid glycine % Recovery	Extraction date
S587 01 AA	Seeds	0.01	75.6%	-	26/01/2023
S587 01 BA	Seeds	0.10	91.7%	-	27/01/2023
S587 01 CA	Seeds	0.01	-	61.5%	27/01/2023
S587 01 DA	Seeds	0.10	-	71.0%	26/01/2023

### Results

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2121 BP1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2121 01 01	C2121 BP1 / UH / A	-	Seeds	-	NDR
C2121 01 02	C2121 BP1 / TH / A	FAWORYT 300 SL	Seeds	69	0.04

DAA: Days After Application

NDR: No detectable residues (residues below the limit of detection)

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

### A 2.1.3.1.1.13 Study 13

Reference:	KCA 6.3/13
Report	Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Oilseed Rape Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022, E. Thomas-Delille, 2023, C2122, Anadiag, France
Guideline(s):	Regulation (EC) No. 1107/2009 Regulation (EU) No. 283/2013 and 284/2013 2004/10/EC GLP Directive OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021 SANTE/2019/12752 - Technical guidelines on data requirements for setting

Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin.

SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes

OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.

**Deviations:**

**Deviation No. 25/04/2022**

The growth stage at application No.1 on 22/04/2022 was BBCH 52-53 instead of BBCH 51 required by the study plan. The application could not be performed earlier due to rainy weather from 19/04/2022 to 21/04/2022. No impact is expected as BBCH 52-53 is very close to BBCH 51 (flower buds are still closed and tight).

**Deviation No. 03/05/2022**

The growth stage at sampling No.2 on 02/05/2022 was BBCH 59-60 instead of BBCH 59 required by the study plan. Acceleration of the crop development due to the increase of the temperatures. No impact as only 5-10 % of the plants have reached BBCH 60.

**GLP:**

Yes

**Acceptability:**

Yes

**Objective of the study**

The objective of the study was to determine the residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in Oilseed Rape raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at one site in Northern Europe. The trial was sampled frequently to monitor the decline of residues shortly after the treatment.

One plot was treated once with CHR/H/CPD 300 SL at BBCH 52-53\*, at the application rate of 0.4 L/ha (120 g clopyralid/ha) with the adjuvant Asystent+ at the rate of 0.1 L/ha.

One plot remained untreated.

Samplings were performed at 0 DBA (day before application) on untreated plot and at 0 DAA (days after application) on the treated plot, then treated plot was sampled at BBCH 59-60\*\*, BBCH 69 and at BBCH 79. At BBCH 89 (at maturity of the crop) untreated and treated plots were sampled.

Clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) residues were analysed in samples harvested during the field phase.

\*see deviation No.25/04/2022

\*\*see deviation No.03/05/2022

**Field phase description**

The objective of the study was to determine the residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in Oilseed Rape raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The following pattern was designed for the treatments and the samplings:

#### 1.1.1.1 Application details

Plot	Test Item	App. No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	<b>CHR/H/CPD 300 SL</b>	T1	BBCH 51	0.4 L/ha	120 g/ha	200-300 L/ha (±10%)
	<b>Asystent+*</b>			0.1 L/ha	-	

\*Adjuvant (Asystent+) to be added in the tank mix with the test item

#### 1.1.1.2 Sampling Details

##### Decline curve trial

Sampling event	Plot	Timing	Matrix	Min. Sample size
<b>S1</b>	U	<b>0 DBA</b>	Whole plants	0.5 kg
	T	<b>0 DAA</b>	Whole plants	0.5 kg
<b>S2</b>	T	BBCH 59	Whole plants	0.5 kg
<b>S3</b>	T	BBCH 69	Whole plants	0.5 kg
<b>S4</b>	T	BBCH 79	Whole plants	1kg
<b>S5</b>	U, T	BBCH 89 (NCH)	Seeds	<b>2 kg</b>

DBA : Days Before Application

DAA : Days After Application

NCH: Normal Commercial Harvest

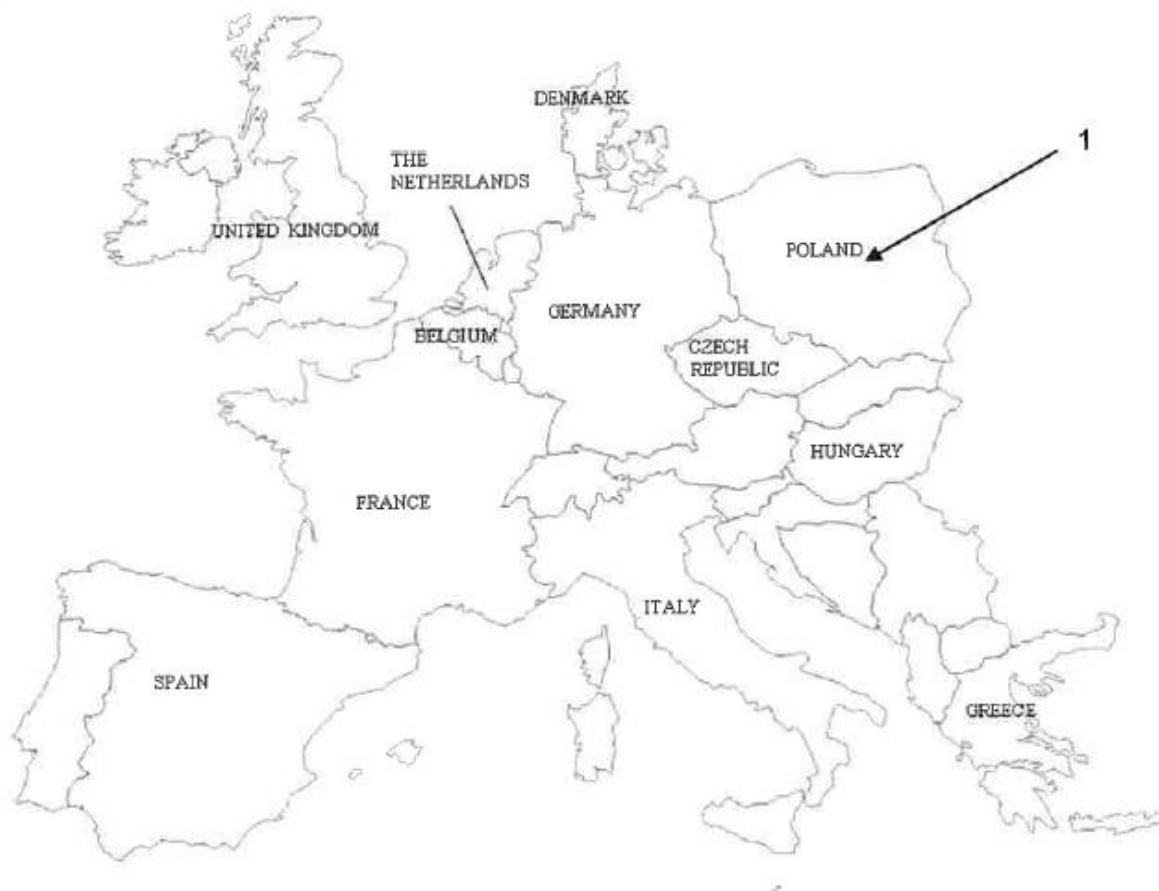
#### Location of the trial

The trial was performed on soil type and under cultural practices typical for oilseed rape production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Type of trial	Crop	European area	Region Country
1	<b>C2122 PL1</b>	Krzysztof NOWAK	DC	Oilseed Rape	North	Lodzkie, Poland

DC: Decline curve

## Location



## Identity and composition of the test item(s):

### Test item

Trade or Code Name	CHR/H/CPD 300 SL
Active substance (a.s.)	Clopyralid
Formulation type	SL
CAS Number	[1702-17-6]
Nominal content of a.s.	300 g/L (expressed as clopyralid)
Batch number*	02/2018
Actual content *	30.18 %
Expiry date*	31/12/2022

## General Information on the trial

### Crop and soil Information

Trial No.	Crop	Variety	Crop density (kg/ha)	Sowing / Planting date	Soil type	pH	Organic matter (%)
C2122 PL1	Oilseed Rape	GALILEUS	3.2	28/08/2021	Sandy clay loam	6.5	1.5

## Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (m)	Pressure (bars)
C2122 PL1	EUROPULVE	Flat fan	Teejet XR 110 02 VS	3.0	9	0.33	3.0

#### Summary of the actual application(s) data

Trial No.	Plot	Application No.	a.s. rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2122 PL1	T	1	118.4	-1.3	296	22/04/2022	52-53*

a.s.: active substance

\*see deviation No.25/04/2022

#### Sampling of specimens

Trial No	Sampling	Actual Date	Actual DAA	Actual Growth Stage (BBCH)
C2122 PL1	1	22/04/2022	0 DBA / 0 DAA	52-53
	2	02/05/2022	10	59-60*
	3	23/05/2022	31	69
	4	23/06/2022	62	79
	5	20/07/2022	89	89

DAA: Days After Application

DBA: Days Before Application

\*see deviation No.03/05/2022

#### ANALYTICAL PHASE

The objective of the analytical phase was to determine the residue levels of clopyralid in samples harvested during the field phase.

#### Experimental details

##### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trial.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table::



#### TRIAL No. C2122 PL1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2122 01 01	C2122 PL1 / U0 / A	22/04/2022	02/02/2023	286	04/02/2023	2
C2122 01 02	C2122 PL1 / T0 / A	22/04/2022	02/02/2023	286	05/02/2023	3
C2122 01 03	C2122 PL1 / T59 / A	02/05/2022	02/02/2023	276	05/02/2023	3
C2122 01 04	C2122 PL1 / T69 / A	23/05/2022	02/02/2023	255	05/02/2023	3
C2122 01 05	C2122 PL1 / T79 / A	23/06/2022	02/02/2023	224	05/02/2023	3
C2122 01 06	C2122 PL1 / UH / A	20/07/2022	26/01/2023	190	04/02/2023	9
C2122 01 07	C2122 PL1 / TH / A	20/07/2022	26/01/2023	190	04/02/2023	9

\*Frozen storage time of samples from sampling to extraction (days)

\*\*Refrigerated storage time of final extracts, from extraction to analysis (days)

#### Storage stability of specimens

Specimens were stored frozen for no more than 286 days from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in commodities with high water, high oil, high acid and dry/high starch content (EFSA Journal Volume19, Issue1, January 2021, e06389).

#### Storage stability of extracts

After extraction, samples were stored refrigerated and analysed after maximum 3 days for whole plant and 9 days for seeds.

Results of storage stability of extracts in ANADIAG validation study No. C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities” showed a good stability of clopyralid residues for up to 15 days of refrigerated storage for high water content and 19 days of refrigerated storage for high oil content.

#### Specimen preparation

The specimens were prepared according to ANADIAG SOPs.

The sample was blended with dry ice and placed for at least 12 hours at  $T < -18^{\circ}\text{C}$  for sublimation of dry ice. The amount required by the analytical method (2 g) was weighed from this homogeneous matrix.

#### Specimen analysis

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

##### Outline of ANADIAG method:

Residues of clopyralid and its conjugates are extracted and hydrolysed from samples by heating at  $60^{\circ}\text{C}$  for 3 hours with 2.5M KOH. After acidification with  $\text{H}_2\text{SO}_4$ , addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract is purified with a liquid-liquid partition. An aliquot of the upper layer is evaporated to dryness and the sample is reconstituted in 50:50, methanol/ $\text{H}_2\text{O}$  + 0.1% formic acid. Extracts are analysed by LC-MS/MS.

ANADIAG References (French version) of the method are  
for the preparation and extraction of the samples:  
for the analysis of extracts and for the calibration:

**SOP MP 718**  
**SOP MA 1809**

#### LOD

The limit of detection (LOD) was expressed as lowest calibration standard.

The LOD was 0.4 ng/mL for clopyralid in high water content (corresponding to 0.002 mg/kg for clopyralid and 0.003 mg/kg for clopyralid glycine).

## LOQ

The LOQ was 0.01 mg/kg for clopyralid and clopyralid glycine in high water content.

### Preparation of standard solutions

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

	Solvent	Concentration	Storage conditions	Expiry date (Preparation + ...)
Stock solution Clopyralid	Acetonitrile	≈ 1 mg/mL	Frozen	6 months
Stock solution Clopyralid glycine	Methanol	≈ 1 mg/mL	Frozen	6 months
Spiking solutions All analyte separately	Acetonitrile	≈ 0.2 and 2 µg/mL	Frozen	1 month
Intermediate calibration solutions Clopyralid <sup>(1)</sup>	Control extract	≈ 200 and 20 ng/mL	Refrigerated	14 days
Matrix-matched Calibration solutions Clopyralid <sup>(1)</sup>	Control extract	≈ 0.4 to 24 ng/mL	Refrigerated	14 days
Intermediate calibration solutions Clopyralid <sup>(2)</sup>	Methanol / water (50/50) + 0.1% formic acid	≈ 200 and 20 ng/mL	Refrigerated	14 days
Calibration solution Clopyralid <sup>(2)</sup>	Methanol / water (50/50) + 0.1% formic acid	≈ 0.4 to 24 ng/mL	Refrigerated	14 days

<sup>(1)</sup> For analysis of undiluted extracts

<sup>(2)</sup> For analysis of diluted extracts

### Calibration curves

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas of clopyralid obtained from chromatograms were plotted versus concentration and the calibration functions were determined by least square fit.

Number and concentrations of standards used, as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve ( $r$ ) should be  $\geq 0.990$  for the calibration to be acceptable with regression residuals randomly distributed.

All extracts analysed (after dilution when required) fell within the range of the standard curve.

### Fortification procedure

Fortifications were performed by adding known amounts of the spiking solutions to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

The spiked samples for whole plant and seeds were done on untreated samples available at ANADIAG laboratory (ANADIAG sample No. S592 for whole plant and S587 for seeds). The absence of the analyte in these samples was checked within this study. The amount found was not detectable.

The recoveries of the spiked samples met with the acceptance criteria described in SANTE/2020/12830, Rev.1.



Analytical Sample No.	Matrix	Fortification level (mg/kg)	Clopyralid % Recovery	Clopyralid glycine % Recovery	Extraction date
S592 01 AA	Whole plant	0.01	68.2%	-	02/02/2023
S592 01 BA	Whole plant	0.10	96.3%	-	03/02/2023
S592 01 CA	Whole plant	0.01	-	70.1%	03/02/2023
S592 01 DA	Whole plant	0.10	-	76.9%	02/02/2023
S592 01 EA D200	Whole plant	20	106.7%	-	02/02/2023
S592 01 FA D200	Whole plant	20	-	78.5%	02/02/2023
S587 01 AA	Seeds	0.01	75.6%	-	26/01/2023
S587 01 BA	Seeds	0.10	91.7%	-	27/01/2023
S587 01 CA	Seeds	0.01	-	61.5%	27/01/2023
S587 01 DA	Seeds	0.10	-	71.0%	26/01/2023

## Results

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2122 PL1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2122 01 01	C2122 PL1 / U0 / A	-	Whole plants	-	NDR
C2122 01 02	C2122 PL1 / T0 / A	CHR/H/CPD 300 SL	Whole plants	0	2.33
C2122 01 03	C2122 PL1 / T59 / A	CHR/H/CPD 300 SL	Whole plants	10	1.70
C2122 01 04	C2122 PL1 / T69 / A	CHR/H/CPD 300 SL	Whole plants	31	1.01
C2122 01 05	C2122 PL1 / T79 / A	CHR/H/CPD 300 SL	Whole plants	62	1.02
C2122 01 06	C2122 PL1 / UH / A	-	Seeds	-	NDR
C2122 01 07	C2122 PL1 / TH / A	CHR/H/CPD 300 SL	Seeds	89	0.04

DAA: Days After Application

NDR: No detectable residues (residues below the limit of detection)

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

### A 2.1.3.1.1.14 Study 14

Reference: KCA 6.3/14

Report Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Oilseed Rape Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022, E. Thomas-Delille, 2023, C2123, Anadiag, France

Guideline(s): Regulation (EC) No. 1107/2009  
Regulation (EU) No. 283/2013 and 284/2013  
2004/10/EC GLP Directive  
OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021  
SANTE/2019/12752 - Technical guidelines on data requirements for setting

Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin.  
SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes  
OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.

Deviations:	No
GLP:	Yes
Acceptability:	Yes

### Objective of the study

The objective of the study was to determine the residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in Oilseed Rape raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at one site in Northern Europe. The trial was sampled at harvest.

One plot was treated once with CHR/H/CPD 300 SL at BBCH 51, at the application rate of 0.4 L/ha (120 g clopyralid/ha) with the adjuvant Asystent+ at the rate of 0.1 L/ha.

One plot remained untreated.

Sampling was performed at BBCH 89 (at maturity of the crop) in untreated and treated plots.

Clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) residues were analysed in samples harvested during the field phase.

### Field phase description

The objective of the study was to determine the residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in Oilseed Rape raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

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The following pattern was designed for the treatments and the samplings:

#### 1.1.1.1 Application details

Plot	Test Item	App. No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	CHR/H/CPD 300 SL	T1	BBCH 51	0.4 L/ha	120 g/ha	200-300 L/ha (±10%)
	Asystent+*			0.1 L/ha	-	

\*Adjuvant (Asystent+) to be added in the tank mix with the test item

#### 1.1.1.2 Sampling Details

##### Residue at harvest

Sampling event	Plot	Timing	Matrix	Min. Sample size
S1	U, T	BBCH 89 (NCH)	Seeds	2 kg

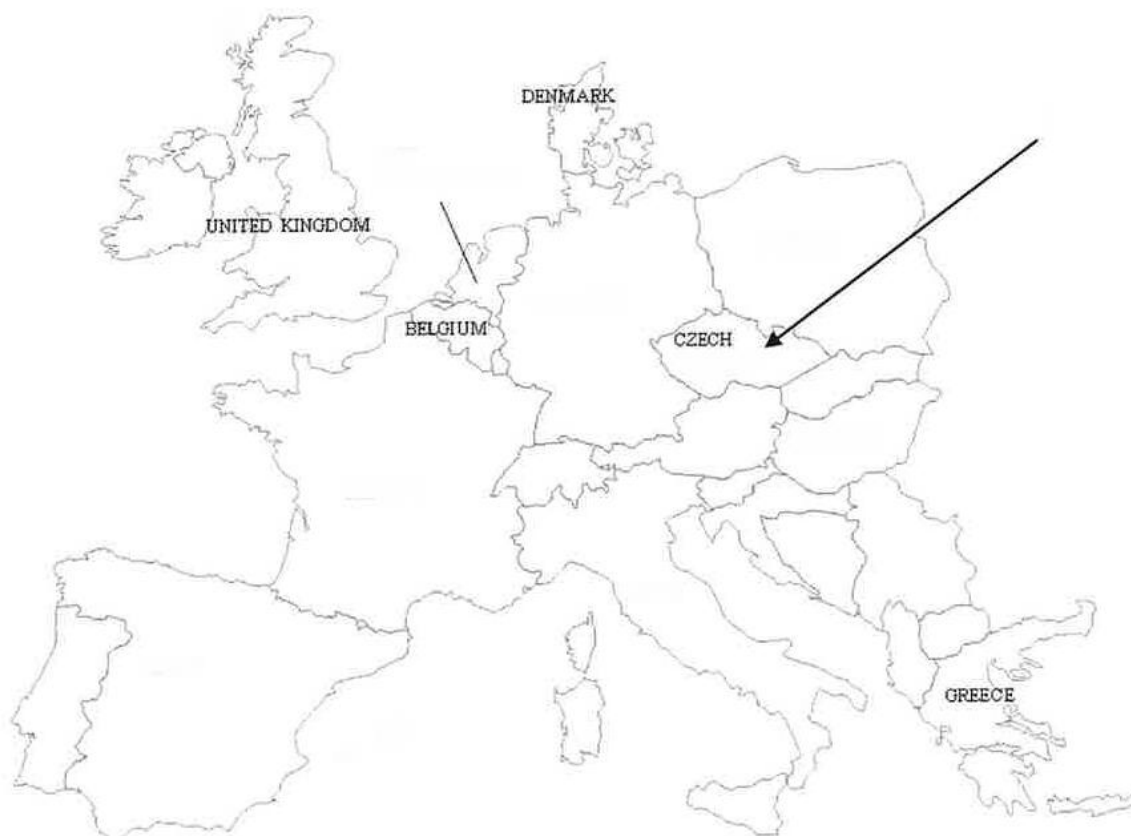
NCH: Normal Commercial Harvest

#### Location of the trial

The trial was performed on soil type and under cultural practices typical for oilseed rape production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Type of trial	Crop	European area	Region Country
1	C2123 CZ1	Iva SIMEK	RH	Oilseed Rape	North	Pardubice, Czech Republic

RH: Residue at Harvest



## Identity and composition of the test item(s):

### Test item

<b>Trade or Code Name</b>	<b>CHR/H/CPD 300 SL</b>
<b>Active substance (a.s.)</b>	Clopyralid
<b>Formulation type</b>	SL
<b>CAS Number</b>	[1702-17-6]
<b>Nominal content of a.s.</b>	300 g/L (expressed as clopyralid)
<b>Batch number*</b>	02/2018
<b>Actual content *</b>	30.18 %
<b>Expiry date*</b>	31/12/2022

## General Information on the trial

### Crop and soil Information

Trial No.	Crop	Variety	Crop density (kg/ha)	Sowing / Planting date	Soil type	pH	Organic matter (%)
<b>C2123 CZ1</b>	Oilseed Rape	TEMPTATION	3	19/08/2021	Clay	6.0	2.1

### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (m)	Pressure (bars)
<b>C2123 CZ1</b>	PULVEXPER	Flat fan	Teejet XR 110 015 VS	3	9	0.33	2

### Summary of the actual application(s) data

Trial No.	Plot	Application No.	a.s. rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
<b>C2123 CZ1</b>	T	1	115.2	-4.0	240	20/04/2022	51

a.s.: active substance

### Sampling of specimens

Trial No	Sampling	Actual Date	Actual DAA	Actual Growth Stage (BBCH)
<b>C2123 CZ1</b>	<b>1</b>	21/07/2022	92	89

DAA: Days After Application

## ANALYTICAL PHASE

The objective of the analytical phase was to determine the residue levels of clopyralid in samples harvested during the field phase.

### Experimental details

#### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trial.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table::

**TRIAL No. C2123 CZ1**

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2123 01 01	C2123 CZ1 / UH / A	21/07/2022	27/01/2023	190	04/02/2023	8
C2123 01 02	C2123 CZ1 / TH / A	21/07/2022	27/01/2023	190	04/02/2023	8

\*Frozen storage time of samples from sampling to extraction (days)

\*\*Refrigerated storage time of final extracts, from extraction to analysis (days)

**Storage stability of specimens**

Specimens were stored frozen for no more than 190 days from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in commodities with high water, high oil, high acid and dry/high starch content (EFSA Journal Volume19, Issue1, January 2021, e06389).

**Storage stability of extracts**

After extraction, samples were stored refrigerated and analysed after maximum 8 days for seeds.

Results of storage stability of extracts in ANADIAG validation study No. C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities” showed a good stability of clopyralid residues for up to 19 days of refrigerated storage for high oil content.

**Specimen preparation**

The specimens were prepared according to ANADIAG SOPs.

The sample was blended with dry ice and placed for at least 12 hours at  $T < -18^{\circ}\text{C}$  for sublimation of dry ice. The amount required by the analytical method (2 g) was weighed from this homogeneous matrix.

**Specimen analysis**

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

Outline of ANADIAG method:

Residues of clopyralid and its conjugates are extracted and hydrolysed from samples by heating at  $60^{\circ}\text{C}$  for 3 hours with 2.5M KOH. After acidification with  $\text{H}_2\text{SO}_4$ , addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract is purified with a liquid-liquid partition. An aliquot of the upper layer is evaporated to dryness and the sample is reconstituted in 50:50, methanol/ $\text{H}_2\text{O}$  + 0.1% formic acid. Extracts are analysed by LC-MS/MS.

ANADIAG References (French version) of the method are  
for the preparation and extraction of the samples:  
for the analysis of extracts and for the calibration:

**SOP MP 718**  
**SOP MA 1809**

**LOD**

The limit of detection (LOD) was expressed as lowest calibration standard.

The LOD was 0.4 ng/mL for clopyralid in high water content (corresponding to 0.002 mg/kg for clopyralid and 0.003 mg/kg for clopyralid glycine).

**LOQ**

The LOQ was 0.01 mg/kg for clopyralid and clopyralid glycine in high water content.

**Preparation of standard solutions**

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

	Solvent	Concentration	Storage conditions	Expiry date (Preparation + ...)
<b>Stock solution Clopyralid</b>	Acetonitrile	≈ 1 mg/mL	Frozen	6 months
<b>Stock solution Clopyralid glycine</b>	Methanol	≈ 1 mg/mL	Frozen	6 months
<b>Spiking solutions All analyte separately</b>	Acetonitrile	≈ 0.2 and 2 µg/mL	Frozen	1 month
<b>Intermediate calibration solutions Clopyralid</b>	Control extract	≈ 200 and 20 ng/mL	Refrigerated	14 days
<b>Matrix-matched Calibration solutions Clopyralid</b>	Control extract	≈ 0.4 to 24 ng/mL	Refrigerated	14 days

### Calibration curves

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas of clopyralid obtained from chromatograms were plotted versus concentration and the calibration functions were determined by least square fit.

Number and concentrations of standards used, as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve ( $r$ ) should be  $\geq 0.990$  for the calibration to be acceptable with regression residuals randomly distributed.

All extracts analysed fell within the range of the standard curve.

### Fortification procedure

Fortifications were performed by adding known amounts of the spiking solutions to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

The spiked samples seeds were done on untreated samples available at ANADIAG laboratory (ANADIAG sample No.S587 for seeds). The absence of the analyte in these samples was checked within this study. The amount found was not detectable.

The recoveries of the spiked samples met with the acceptance criteria described in SANTE/2020/12830, Rev.1.

Analytical Sample No.	Matrix	Fortification level (mg/kg)	Clopyralid % Recovery	Clopyralid glycine % Recovery	Extraction date
S587 01 AA	Seeds	0.01	75.6%	-	26/01/2023
S587 01 BA	Seeds	0.10	91.7%	-	27/01/2023
S587 01 CA	Seeds	0.01	-	61.5%	27/01/2023
S587 01 DA	Seeds	0.10	-	71.0%	26/01/2023

### Results

The analytical results obtained are summarized in the table below.



**Table 1 TRIAL No. C2123 CZ1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2123 01 01	C2123 CZ1 / TH / A	-	Seeds	-	NDR
C2123 01 02	C2123 CZ1 / TH / A	CHR/H/CPD 300 SL	Seeds	92	< LOQ

DAA: Days After Application

NDR: No detectable residues (residues below the limit of detection)

< LOQ: Residues between LOD and LOQ

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

#### A 2.1.3.1.1.15 Study 15

Reference:	KCA 6.3/15
Report	Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Oilseed Rape Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022, E. Thomas-Delille, 2023, C2124, Anadiag, France
Guideline(s):	Regulation (EC) No. 1107/2009 Regulation (EU) No. 283/2013 and 284/2013 2004/10/EC GLP Directive OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021 SANTE/2019/12752 - Technical guidelines on data requirements for setting Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin. SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.
Deviations:	<b>Deviation No. 28/11/2022</b> During the shipment, the temperature was above -18°C for 10h10 at total on 23-24/11/2022 with a maximum at -7.5 °C on 24/11/2022. The temperature was between -13°C and -5°C for 7h15 instead of a maximum duration of 3h allowed by the study plan. The following samples are concerned by this deviation: C2124 CZ1 / UH / R and C2124 CZ1 / TH / R. Technical issue with the freezer truck during connection to the electrical network overnight at a test site. No impact on the trial as the analytical samples were shipped in good conditions and the spare specimens were not analysed.
GLP:	Yes
Acceptability:	Yes

#### Objective of the study

The objective of the study was to determine the residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in Oilseed Rape raw agricultural commodity (RAC)

after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at one site in Northern Europe. The trial was sampled frequently to monitor the decline of residues shortly after the treatment.

One plot was treated once with CHR/H/CPD 300 SL at BBCH 51, at the application rate of 0.4 L/ha (120 g clopyralid/ha) with the adjuvant Asystent+ at the rate of 0.1 L/ha.

One plot remained untreated.

Samplings were performed at 0 DBA (day before application) on untreated plot and at 0 DAA (days after application) on the treated plot, then treated plot was sampled at BBCH 59, BBCH 69 and at BBCH 79. At BBCH 89 (at maturity of the crop) untreated and treated plots were sampled.

Clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) residues were analysed in samples harvested during the field phase.

### Field phase description

The objective of the study was to determine the residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in Oilseed Rape raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The following pattern was designed for the treatments and the samplings:

#### 1.1.1.1 Application details

Plot	Test Item	App. No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	<b>CHR/H/CPD 300 SL</b>	T1	BBCH 51	0.4 L/ha	120 g/ha	200-300 L/ha (±10%)
	<b>Asystent+*</b>			0.1 L/ha	-	

\*Adjuvant (Asystent+) to be added in the tank mix with the test item

#### 1.1.1.2 Sampling Details

##### Decline curve trial

Sampling event	Plot	Timing	Matrix	Min. Sample size
<b>S1</b>	U	<b>0 DBA</b>	Whole plants	0.5 kg
	T	<b>0 DAA</b>	Whole plants	0.5 kg
<b>S2</b>	T	BBCH 59	Whole plants	0.5 kg
<b>S3</b>	T	BBCH 69	Whole plants	0.5 kg
<b>S4</b>	T	BBCH 79	Whole plants	1kg
<b>S5</b>	U, T	<b>BBCH 89 (NCH)</b>	Seeds	<b>2 kg</b>

DBA : Days Before Application

DAA : Days After Application

NCH: Normal Commercial Harvest

### Location of the trial

The trial was performed on soil type and under cultural practices typical for oilseed rape production and on a typical cultivar of the regional commercial production.



	Trial No.	Principal Investigator	Type of trial	Crop	European area	Region Country
1	C2124 CZ1	Iva SIMEK	DC	Oilseed Rape	North	Hradec Kralove, Czech Republic

DC: Decline curve



#### Identity and composition of the test item(s):

##### Test item

Trade or Code Name	CHR/H/CPD 300 SL
Active substance (a.s.)	Clopyralid
Formulation type	SL
CAS Number	[1702-17-6]
Nominal content of a.s.	300 g/L (expressed as clopyralid)
Batch number*	02/2018
Actual content *	30.18 %
Expiry date*	31/12/2022

#### General Information on the trial

##### Crop and soil Information

Trial No.	Crop	Variety	Crop density (kg/ha)	Sowing / Planting date	Soil type	pH	Organic matter (%)
C2124 CZ1	Oilseed Rape	AGANOS	3	21/08/2021	Loam	5.8	2.9

##### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (m)	Pressure (bars)
<b>C2124 CZ1</b>	PULVEXPER	Flat fan	Teejet XR 110 015 VS	3	9	0.33	2

#### Summary of the actual application(s) data

Trial No.	Plot	Application No.	a.s. rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
<b>C2124 CZ1</b>	T	1	116.3	-3.1	242	26/04/2022	51

a.s.: active substance

#### Sampling of specimens

Trial No	Sampling	Actual Date	Actual DAA	Actual Growth Stage (BBCH)
<b>C2124 CZ1</b>	1	26/04/2022	0 DBA / 0 DAA	51
	2	07/05/2022	11	59
	3	27/05/2022	31	69
	4	22/06/2022	57	79
	5	23/07/2022	88	89

DAA: Days After Application

DBA: Days Before Application

#### ANALYTICAL PHASE

The objective of the analytical phase was to determine the residue levels of clopyralid in samples harvested during the field phase.

#### Experimental details

##### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trial.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table::

#### TRIAL No. C2124 CZ1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2124 01 01	C2124 CZ1 / U0 / A	26/04/2022	03/02/2023	283	04/02/2023	1
C2124 01 02	C2124 CZ1 / T0 / A	26/04/2022	03/02/2023	283	05/02/2023	2
C2124 01 03	C2124 CZ1 / T59 / A	07/05/2022	03/02/2023	272	05/02/2023	2
C2124 01 04	C2124 CZ1 / T69 / A	27/05/2022	03/02/2023	252	05/02/2023	2
C2124 01 05	C2124 CZ1 / T79 / A	22/06/2022	03/02/2023	226	05/02/2023	2
C2124 01 06	C2124 CZ1 / UH / A	23/07/2022	27/01/2023	188	04/02/2023	8
C2124 01 07	C2124 CZ1 / TH / A	23/07/2022	27/01/2023	188	04/02/2023	8

\*Frozen storage time of samples from sampling to extraction (days)

\*\*Refrigerated storage time of final extracts, from extraction to analysis (days)

#### Storage stability of specimens

Specimens were stored frozen for no more than 283 days from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in commodities with high water, high oil, high acid and dry/high starch content (EFSA Journal Volume19, Issue1, January 2021, e06389).

#### Storage stability of extracts

After extraction, samples were stored refrigerated and analysed after maximum 2 days for whole plant and 8 days for seeds.

Results of storage stability of extracts in ANADIAG validation study No. C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities” showed a good stability of clopyralid residues for up to 15 days of refrigerated storage for high water content and 19 days of refrigerated storage for high oil content.

#### Specimen preparation

The specimens were prepared according to ANADIAG SOPs.

The sample was blended with dry ice and placed for at least 12 hours at  $T < -18^{\circ}\text{C}$  for sublimation of dry ice. The amount required by the analytical method (2 g) was weighed from this homogeneous matrix.

#### Specimen analysis

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

##### Outline of ANADIAG method:

Residues of clopyralid and its conjugates are extracted and hydrolysed from samples by heating at  $60^{\circ}\text{C}$  for 3 hours with 2.5M KOH. After acidification with  $\text{H}_2\text{SO}_4$ , addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract is purified with a liquid-liquid partition. An aliquot of the upper layer is evaporated to dryness and the sample is reconstituted in 50:50, methanol/ $\text{H}_2\text{O}$  + 0.1% formic acid. Extracts are analysed by LC-MS/MS.

ANADIAG References (French version) of the method are  
for the preparation and extraction of the samples:  
for the analysis of extracts and for the calibration:

**SOP MP 718**  
**SOP MA 1809**

#### LOD

The limit of detection (LOD) was expressed as lowest calibration standard.

The LOD was 0.4 ng/mL for clopyralid in high water content (corresponding to 0.002 mg/kg for

clopyralid and 0.003 mg/kg for clopyralid glycine).

## LOQ

The LOQ was 0.01 mg/kg for clopyralid and clopyralid glycine in high water content.

## Preparation of standard solutions

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

	Solvent	Concentration	Storage conditions	Expiry date (Preparation + ...)
Stock solution Clopyralid	Acetonitrile	≈ 1 mg/mL	Frozen	6 months
Stock solution Clopyralid glycine	Methanol	≈ 1 mg/mL	Frozen	6 months
Spiking solutions All analyte separately	Acetonitrile	≈ 0.2 and 2 µg/mL	Frozen	1 month
Intermediate calibration solutions Clopyralid <sup>(1)</sup>	Control extract	≈ 200 and 20 ng/mL	Refrigerated	14 days
Matrix-matched Calibration solutions Clopyralid <sup>(1)</sup>	Control extract	≈ 0.4 to 24 ng/mL	Refrigerated	14 days
Intermediate calibration solutions Clopyralid <sup>(2)</sup>	Methanol / water (50/50) + 0.1% formic acid	≈ 200 and 20 ng/mL	Refrigerated	14 days
Calibration solution Clopyralid <sup>(2)</sup>	Methanol / water (50/50) + 0.1% formic acid	≈ 0.4 to 24 ng/mL	Refrigerated	14 days

<sup>(1)</sup> For analysis of undiluted extracts

<sup>(2)</sup> For analysis of diluted extracts

## Calibration curves

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas of clopyralid obtained from chromatograms were plotted versus concentration and the calibration functions were determined by least square fit.

Number and concentrations of standards used, as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve ( $r$ ) should be  $\geq 0.990$  for the calibration to be acceptable with regression residuals randomly distributed.

All extracts analysed (after dilution when required) fell within the range of the standard curve.

## Fortification procedure

Fortifications were performed by adding known amounts of the spiking solutions to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

The spiked samples for whole plant and seeds were done on untreated samples available at ANADIAG laboratory (ANADIAG sample No. S592 for whole plant and S587 for seeds). The absence of the analyte in these samples was checked within this study. The amount found was not detectable.

The recoveries of the spiked samples met with the acceptance criteria described in SANTE/2020/12830, Rev.1.

Analytical Sample No.	Matrix	Fortification level (mg/kg)	Clopyralid % Recovery	Clopyralid glycine % Recovery	Extraction date
S592 01 AA	Whole plant	0.01	68.2%	-	02/02/2023
S592 01 BA	Whole plant	0.10	96.3%	-	03/02/2023
S592 01 CA	Whole plant	0.01	-	70.1%	03/02/2023
S592 01 DA	Whole plant	0.10	-	76.9%	02/02/2023
S592 01 EA D200	Whole plant	20	106.7%	-	02/02/2023
S592 01 FA D200	Whole plant	20	-	78.5%	02/02/2023
S587 01 AA	Seeds	0.01	75.6%	-	26/01/2023
S587 01 BA	Seeds	0.10	91.7%	-	27/01/2023
S587 01 CA	Seeds	0.01	-	61.5%	27/01/2023
S587 01 DA	Seeds	0.10	-	71.0%	26/01/2023

## Results

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2124 CZ1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2124 01 01	C2124 CZ1 / U0 / A	-	Whole plants	-	NDR
C2124 01 02	C2124 CZ1 / T0 / A	CHR/H/CPD 300 SL	Whole plants	0	3.72
C2124 01 03	C2124 CZ1 / T59 / A	CHR/H/CPD 300 SL	Whole plants	11	2.19
C2124 01 04	C2124 CZ1 / T69 / A	CHR/H/CPD 300 SL	Whole plants	31	0.75
C2124 01 05	C2124 CZ1 / T79 / A	CHR/H/CPD 300 SL	Whole plants	57	0.46
C2124 01 06	C2124 CZ1 / UH / A	-	Seeds	-	NDR
C2124 01 07	C2124 CZ1 / TH / A	CHR/H/CPD 300 SL	Seeds	88	0.03

DAA: Days After Application

NDR: No detectable residues (residues below the limit of detection)

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

### A 2.1.3.1.1.16 Study 16

Reference: KCA 6.3/16

Report Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Oilseed Rape Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022, E. Thomas-Delille, 2023, C2125, Anadiag, France

Guideline(s): Regulation (EC) No. 1107/2009  
Regulation (EU) No. 283/2013 and 284/2013  
2004/10/EC GLP Directive  
OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021  
SANTE/2019/12752 - Technical guidelines on data requirements for setting

Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin.  
SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes  
OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.

Deviations: No

GLP: Yes

Acceptability: Yes

### Objective of the study

The objective of the study was to determine the residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in Oilseed Rape raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at one site in Northern Europe. The trial was sampled at harvest.

One plot was treated once with CHR/H/CPD 300 SL at BBCH 51, at the application rate of 0.4 L/ha (120 g clopyralid/ha) with the adjuvant Asystent+ at the rate of 0.1 L/ha.

One plot remained untreated.

Sampling was performed at BBCH 89 (at maturity of the crop) in untreated and treated plots.

Clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) residues were analysed in samples harvested during the field phase.

### Field phase description

The objective of the study was to determine the residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in Oilseed Rape raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

.

The following pattern was designed for the treatments and the samplings:



#### 1.1.1.1 Application details

Plot	Test Item	App. No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	<b>CHR/H/CPD 300 SL</b>	T1	BBCH 51	0.4 L/ha	120 g/ha	200-300 L/ha (±10%)
	<b>Asystent+*</b>			0.1 L/ha	-	

\*Adjuvant (Asystent+) to be added in the tank mix with the test item

#### 1.1.1.2 Sampling Details

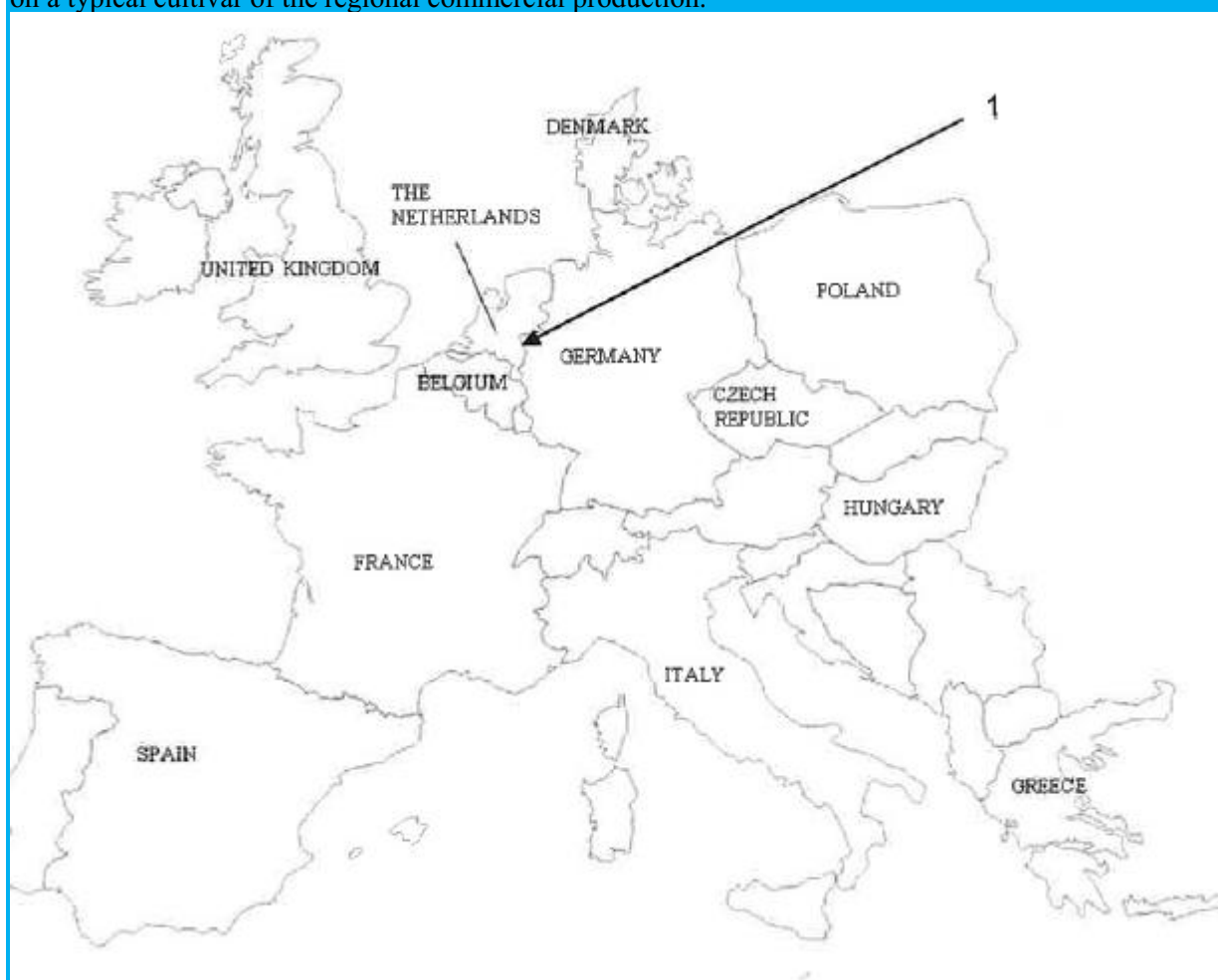
##### Residue at harvest

Sampling event	Plot	Timing	Matrix	Min. Sample size
<b>S1</b>	U, T	BBCH 89 (NCH)	Seeds	<b>2 kg</b>

NCH: Normal Commercial Harvest

#### Location of the trial

The trial was performed on soil type and under cultural practices typical for oilseed rape production and on a typical cultivar of the regional commercial production.



#### Identity and composition of the test item(s):



### Test item

<b>Trade or Code Name</b>	<b>CHR/H/CPD 300 SL</b>
<b>Active substance (a.s.)</b>	Clopyralid
<b>Formulation type</b>	SL
<b>CAS Number</b>	[1702-17-6]
<b>Nominal content of a.s.</b>	300 g/L (expressed as clopyralid)
<b>Batch number*</b>	02/2018
<b>Actual content *</b>	30.18 %
<b>Expiry date*</b>	31/12/2022

### General Information on the trial

#### Crop and soil Information

Trial No.	Crop	Variety	Crop density (kg/ha)	Sowing / Planting date	Soil type	pH	Organic matter (%)
C2125 NL1	Oilseed Rape	ABILITY	3.0	11/04/2022	Sandy loam	6.1	2.6

#### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (m)	Pressure (bars)
C2125 NL1	BAUMANN	Flat fan	Lechler IDK 120-025 POM	3.0	6	0.50	3.0

#### Summary of the actual application(s) data

Trial No.	Plot	Application No.	a.s. rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2125 NL1	T	1	128.9	+7.4	322	23/05/2022	51

a.s.: active substance

#### Sampling of specimens

Trial No	Sampling	Actual Date	Actual DAA	Actual Growth Stage (BBCH)
C2125 NL1	1	03/08/2022	72	89

DAA: Days After Application

### ANALYTICAL PHASE

The objective of the analytical phase was to determine the residue levels of clopyralid in samples harvested during the field phase.

#### Experimental details

##### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trial.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table::

#### TRIAL No. C2125 NL1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2125 01 01	C2125 NL1 / UH / A	03/08/2022	27/01/2023	177	04/02/2023	8
C2125 01 02	C2125 NL1 / TH / A	03/08/2022	27/01/2023	177	04/02/2023	8

\*Frozen storage time of samples from sampling to extraction (days)

\*\*Refrigerated storage time of final extracts, from extraction to analysis (days)

#### Storage stability of specimens

Specimens were stored frozen for no more than 177 days from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in commodities with high water, high oil, high acid and dry/high starch content (EFSA Journal Volume19, Issue1, January 2021, e06389).

#### Storage stability of extracts

After extraction, samples were stored refrigerated and analysed after maximum 8 days for seeds.

Results of storage stability of extracts in ANADIAG validation study No. C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities” showed a good stability of clopyralid residues for up to 19 days of refrigerated storage for high oil content.

#### Specimen preparation

The specimens were prepared according to ANADIAG SOPs.

The sample was blended with dry ice and placed for at least 12 hours at  $T < -18^{\circ}\text{C}$  for sublimation of dry ice. The amount required by the analytical method (2 g) was weighed from this homogeneous matrix.

#### Specimen analysis

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

##### Outline of ANADIAG method:

Residues of clopyralid and its conjugates are extracted and hydrolysed from samples by heating at  $60^{\circ}\text{C}$  for 3 hours with 2.5M KOH. After acidification with  $\text{H}_2\text{SO}_4$ , addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract is purified with a liquid-liquid partition. An aliquot of the upper layer is evaporated to dryness and the sample is reconstituted in 50:50, methanol/ $\text{H}_2\text{O}$  + 0.1% formic acid. Extracts are analysed by LC-MS/MS.

ANADIAG References (French version) of the method are

for the preparation and extraction of the samples:

**SOP MP 718**

for the analysis of extracts and for the calibration:

**SOP MA 1809**

#### LOD

The limit of detection (LOD) was expressed as lowest calibration standard.

The LOD was 0.4 ng/mL for clopyralid in high water content (corresponding to 0.002 mg/kg for clopyralid and 0.003 mg/kg for clopyralid glycine).

#### LOQ

The LOQ was 0.01 mg/kg for clopyralid and clopyralid glycine in high water content.

#### Preparation of standard solutions

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

	Solvent	Concentration	Storage conditions	Expiry date (Preparation + ...)
<b>Stock solution Clopyralid</b>	Acetonitrile	≈ 1 mg/mL	Frozen	6 months
<b>Stock solution Clopyralid glycine</b>	Methanol	≈ 1 mg/mL	Frozen	6 months
<b>Spiking solutions All analyte separately</b>	Acetonitrile	≈ 0.2 and 2 µg/mL	Frozen	1 month
<b>Intermediate calibration solutions Clopyralid</b>	Control extract	≈ 200 and 20 ng/mL	Refrigerated	14 days
<b>Matrix-matched Calibration solutions Clopyralid</b>	Control extract	≈ 0.4 to 24 ng/mL	Refrigerated	14 days

### Calibration curves

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas of clopyralid obtained from chromatograms were plotted versus concentration and the calibration functions were determined by least square fit.

Number and concentrations of standards used, as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve ( $r$ ) should be  $\geq 0.990$  for the calibration to be acceptable with regression residuals randomly distributed.

All extracts analysed within the range of the standard curve.

### Fortification procedure

Fortifications were performed by adding known amounts of the spiking solutions to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

The spiked samples for whole plant and seeds were done on untreated samples available at ANADIAG laboratory (ANADIAG sample No. S592 for whole plant and S587 for seeds). The absence of the analyte in these samples was checked within this study. The amount found was not detectable.

The recoveries of the spiked samples met with the acceptance criteria described in SANTE/2020/12830, Rev.1.

Analytical Sample No.	Matrix	Fortification level (mg/kg)	Clopyralid % Recovery	Clopyralid glycine % Recovery	Extraction date
S587 01 AA	Seeds	0.01	75.6%	-	26/01/2023
S587 01 BA	Seeds	0.10	91.7%	-	27/01/2023
S587 01 CA	Seeds	0.01	-	61.5%	27/01/2023
S587 01 DA	Seeds	0.10	-	71.0%	26/01/2023

### Results

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2125 NL1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2125 01 01	C2125 NL1 / UH / A	-	Seeds	-	NDR
C2125 01 02	C2125 NL1 / TH / A	CHR/H/CPD 300 SL	Seeds	72	< LOQ

DAA: Days After Application

NDR: No detectable residues (residues below the limit of detection)

< LOQ: Residues between LOD and LOQ

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

#### A 2.1.3.1.1.17 Study 17

Reference:	KCA 6.3/17
Report	Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Oilseed Rape Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022, E. Thomas-Delille, 2023, C2126, Anadiag, France
Guideline(s):	Regulation (EC) No. 1107/2009 Regulation (EU) No. 283/2013 and 284/2013 2004/10/EC GLP Directive OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021 SANTE/2019/12752 - Technical guidelines on data requirements for setting Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin. SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.
Deviations:	No
GLP:	Yes
Acceptability:	Yes

#### Objective of the study

The objective of the study was to determine the residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in Oilseed Rape raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at one site in Northern Europe. The trial was sampled frequently to monitor the decline of residues shortly after the treatment.

One plot was treated once with CHR/H/CPD 300 SL at BBCH 51, at the application rate of 0.4 L/ha (120 g clopyralid/ha) with the adjuvant Asystent+ at the rate of 0.1 L/ha.

One plot remained untreated.

Samplings were performed at 0 DBA (day before application) on untreated plot and at 0 DAA (days after application) on the treated plot, then treated plot was sampled at BBCH 59-60\*, BBCH 69 and at BBCH

79. At BBCH 89 (at maturity of the crop) untreated and treated plots were sampled. Clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) residues were analysed in samples harvested during the field phase.

\*At sampling at harvest, only 5-10 % of the plants have reached BBCH 60.

### Field phase description

The objective of the study was to determine the residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in Oilseed Rape raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The following pattern was designed for the treatments and the samplings:

#### 1.1.1.1 Application details

Plot	Test Item	App. No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	CHR/H/CPD 300 SL	T1	BBCH 51	0.4 L/ha	120 g/ha	200-300 L/ha (±10%)
	Asysent+*			0.1 L/ha	-	

\*Adjuvant (Asysent+) to be added in the tank mix with the test item

#### 1.1.1.2 Sampling Details

##### Decline curve trial

Sampling event	Plot	Timing	Matrix	Min. Sample size
S1	U	0 DBA	Whole plants	0.5 kg
	T	0 DAA	Whole plants	0.5 kg
S2	T	BBCH 59	Whole plants	0.5 kg
S3	T	BBCH 69	Whole plants	0.5 kg
S4	T	BBCH 79	Whole plants	1kg
S5	U, T	BBCH 89 (NCH)	Seeds	2 kg

DBA : Days Before Application

DAA : Days After Application

NCH: Normal Commercial Harvest

### Location of the trial

The trial was performed on soil type and under cultural practices typical for oilseed rape production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Type of trial	Crop	European area	Region Country
1	C2126 PL1	Krzysztof NOWAK	DC	Oilseed Rape	North	Lodzkie, Poland

DC: Decline curve

## Location



## Identity and composition of the test item(s):

### Test item

Trade or Code Name	CHR/H/CPD 300 SL
Active substance (a.s.)	Clopyralid
Formulation type	SL
CAS Number	[1702-17-6]
Nominal content of a.s.	300 g/L (expressed as clopyralid)
Batch number*	02/2018
Actual content *	30.18 %
Expiry date*	31/12/2022

## General Information on the trial

### Crop and soil Information

Trial No.	Crop	Variety	Crop density (seeds/m <sup>2</sup> )	Sowing / Planting date	Soil type	pH	Organic matter (%)
C2126 PL1	Oilseed Rape	DUKE	≈ 104	10/09/2021	Sandy clay loam	6.5	1.5

### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (m)	Pressure (bars)
C2126 PL1	EUROPULVE	Flat fan	Teejet XR 110 02 VS	3.0	9	0.33	3.0



### Summary of the actual application(s) data

Trial No.	Plot	Application No.	a.s. rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2126 PL1	T	1	116.0	-3.3	290	27/04/2022	51

a.s.: active substance

### Sampling of specimens

Trial No	Sampling	Actual Date	Actual DAA	Actual Growth Stage (BBCH)
C2126 PL1	1	27/04/2022	0 DBA / 0 DAA	51
	2	02/05/2022	5	59-60*
	3	23/05/2022	26	69
	4	22/06/2022	56	79
	5	27/07/2022	91	89

DAA: Days After Application

DBA: Days Before Application

\*At sampling No.2, only 5-10 % of the plants have reached BBCH 60.

### ANALYTICAL PHASE

The objective of the analytical phase was to determine the residue levels of clopyralid in samples harvested during the field phase.

### Experimental details

#### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trial.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table::

#### TRIAL No. C2126 PL1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2126 01 01	C2126 PL1 / U0 / A	27/04/2022	03/02/2023	282	04/02/2023	1
C2126 01 02	C2126 PL1 / T0 / A	27/04/2022	03/02/2023	282	05/02/2023	2
C2126 01 03	C2126 PL1 / T59 / A	02/05/2022	03/02/2023	277	05/02/2023	2
C2126 01 04	C2126 PL1 / T69 / A	23/05/2022	03/02/2023	256	05/02/2023	2
C2126 01 05	C2126 PL1 / T79 / A	22/06/2022	03/02/2023	226	05/02/2023	2
C2126 01 06	C2126 PL1 / UH / A	27/07/2022	27/01/2023	184	04/02/2023	8
C2126 01 07	C2126 PL1 / TH / A	27/07/2022	27/01/2023	184	04/02/2023	8

\*Frozen storage time of samples from sampling to extraction (days)

\*\*Refrigerated storage time of final extracts, from extraction to analysis (days)



### **Storage stability of specimens**

Specimens were stored frozen for no more than 282 days from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in commodities with high water, high oil, high acid and dry/high starch content (EFSA Journal Volume 19, Issue 1, January 2021, e06389).

### **Storage stability of extracts**

After extraction, samples were stored refrigerated and analysed after maximum 2 days for whole plant and 8 days for seeds.

Results of storage stability of extracts in ANADIAG validation study No. C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities” showed a good stability of clopyralid residues for up to 15 days of refrigerated storage for high water content and 19 days of refrigerated storage for high oil content.

### **Specimen preparation**

The specimens were prepared according to ANADIAG SOPs.

The sample was blended with dry ice and placed for at least 12 hours at  $T < -18^{\circ}\text{C}$  for sublimation of dry ice. The amount required by the analytical method (2 g) was weighed from this homogeneous matrix.

### **Specimen analysis**

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

#### Outline of ANADIAG method:

Residues of clopyralid and its conjugates are extracted and hydrolysed from samples by heating at  $60^{\circ}\text{C}$  for 3 hours with 2.5M KOH. After acidification with  $\text{H}_2\text{SO}_4$ , addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract is purified with a liquid-liquid partition. An aliquot of the upper layer is evaporated to dryness and the sample is reconstituted in 50:50, methanol/ $\text{H}_2\text{O}$  + 0.1% formic acid. Extracts are analysed by LC-MS/MS.

ANADIAG References (French version) of the method are  
for the preparation and extraction of the samples:  
for the analysis of extracts and for the calibration:

**SOP MP 718**  
**SOP MA 1809**

### **LOD**

The limit of detection (LOD) was expressed as lowest calibration standard.

The LOD was 0.4 ng/mL for clopyralid in high water content (corresponding to 0.002 mg/kg for clopyralid and 0.003 mg/kg for clopyralid glycine).

### **LOQ**

The LOQ was 0.01 mg/kg for clopyralid and clopyralid glycine in high water content.

### **Preparation of standard solutions**

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

	<b>Solvent</b>	<b>Concentration</b>	<b>Storage conditions</b>	<b>Expiry date (Preparation + ...)</b>
<b>Stock solution Clopyralid</b>	Acetonitrile	≈ 1 mg/mL	Frozen	6 months
<b>Stock solution Clopyralid glycine</b>	Methanol	≈ 1 mg/mL	Frozen	6 months
<b>Spiking solutions All analyte separately</b>	Acetonitrile	≈ 0.2 and 2 µg/mL	Frozen	1 month
<b>Intermediate calibration solutions Clopyralid<sup>(1)</sup></b>	Control extract	≈ 200 and 20 ng/mL	Refrigerated	14 days
<b>Matrix-matched Calibration solutions Clopyralid<sup>(1)</sup></b>	Control extract	≈ 0.4 to 24 ng/mL	Refrigerated	14 days
<b>Intermediate calibration solutions Clopyralid<sup>(2)</sup></b>	Methanol / water (50/50) + 0.1% formic acid	≈ 200 and 20 ng/mL	Refrigerated	14 days
<b>Calibration solution Clopyralid<sup>(2)</sup></b>	Methanol / water (50/50) + 0.1% formic acid	≈ 0.4 to 24 ng/mL	Refrigerated	14 days

<sup>(1)</sup> For analysis of undiluted extracts

<sup>(2)</sup> For analysis of diluted extracts

### Calibration curves

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas of clopyralid obtained from chromatograms were plotted versus concentration and the calibration functions were determined by least square fit.

Number and concentrations of standards used, as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve (r) should be  $\geq 0.990$  for the calibration to be acceptable with regression residuals randomly distributed.

All extracts analysed (after dilution when required) fell within the range of the standard curve.

### Fortification procedure

Fortifications were performed by adding known amounts of the spiking solutions to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

The spiked samples for whole plant and seeds were done on untreated samples available at ANADIAG laboratory (ANADIAG sample No. S592 for whole plant and S587 for seeds). The absence of the analyte in these samples was checked within this study. The amount found was not detectable.

The recoveries of the spiked samples met with the acceptance criteria described in SANTE/2020/12830, Rev.1.

Analytical Sample No.	Matrix	Fortification level (mg/kg)	Clopyralid % Recovery	Clopyralid glycine % Recovery	Extraction date
S592 01 AA	Whole plant	0.01	68.2%	-	02/02/2023
S592 01 BA	Whole plant	0.10	96.3%	-	03/02/2023
S592 01 CA	Whole plant	0.01	-	70.1%	03/02/2023
S592 01 DA	Whole plant	0.10	-	76.9%	02/02/2023
S592 01 EA D200	Whole plant	20	106.7%	-	02/02/2023
S592 01 FA D200	Whole plant	20	-	78.5%	02/02/2023
S587 01 AA	Seeds	0.01	75.6%	-	26/01/2023
S587 01 BA	Seeds	0.10	91.7%	-	27/01/2023
S587 01 CA	Seeds	0.01	-	61.5%	27/01/2023
S587 01 DA	Seeds	0.10	-	71.0%	26/01/2023

## Results

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2126 PL1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2126 01 01	C2126 PL1 / U0 / A	-	Whole plants	-	NDR
C2126 01 02	C2126 PL1 / T0 / A	CHR/H/CPD 300 SL	Whole plants	0	2.15
C2126 01 03	C2126 PL1 / T59 / A	CHR/H/CPD 300 SL	Whole plants	5	2.02
C2126 01 04	C2126 PL1 / T69 / A	CHR/H/CPD 300 SL	Whole plants	26	1.04
C2126 01 05	C2126 PL1 / T79 / A	CHR/H/CPD 300 SL	Whole plants	56	0.53
C2126 01 06	C2126 PL1 / UH / A	-	Seeds	-	NDR
C2126 01 07	C2126 PL1 / TH / A	CHR/H/CPD 300 SL	Seeds	91	0.01

DAA: Days After Application

NDR: No detectable residues (residues below the limit of detection)

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

March 2024

Wheat

The objective of the studies were to determine the residue levels of Clopyralid (Sum of Clopyralid, its salts and conjugates) in winter wheat raw agricultural commodity (RAC) after one foliar application (at BBCH 29) of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha. Eight independent trials (Czech Republic, Germany, Poland and France) are accepted and valid in relation to storage stability data. Residues are below MRL established for wheat (Reg. (EU) 2021/1807).

Note: The maps presented in the studies do not contain the correct locations of the studies.

#### A 2.1.3.1.1.18 Study 18

Reference:	KCA 6.3/18
Report	Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Winter Wheat Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022, E. Schneider, 2023, C2114, Anadiag, France
Guideline(s):	Regulation (EC) No. 1107/2009 Regulation (EU) No. 283/2013 and 284/2013 2004/10/EC GLP Directive OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021 SANTE/2019/12752 - Technical guidelines on data requirements for setting Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin. SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.
Deviations:	Deviation No. 08/07/2022 Trial C2114 BW1 : Description: 1 - At S5 (last sampling at maturity), the interval between sampling and freezing was upper to the 24 hours allowed in the study plan for samples: - C2114 BW1 / UHG / A and C2114 BW1 / UHG / R : 24h55 2 - The weight of sample C2114 BW1 / THG / R is 0.922 kg instead of minimum 1 kg as requested in the study plan Reason: 1 - Due to the dry summer, all the trials were harvested on same time, and it was not possible to respect the 24 hours between sampling and freezing. 2 - The collected ears provided a grain yield too low. Impact: The deviation has no impact on the study as 1 - 24h55 is close to 24h00 and as it is an untreated sample. 2 - 0.922 kg grain is representative (sample taken from >50 plants from >12 places) from the plot, and retain sample was not analysed.
GLP:	Yes
Acceptability:	Yes

### Objective of the study

The objective of the study was to determine the residue levels of Clopyralid (Sum of Clopyralid, its salts and conjugates) in Winter wheat raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at 1 site in Northern Europe. The trial was sampled frequently to monitor the decline of residues shortly after the treatment.

One plot was treated once with CHR/H/CPD 300 SL at BBCH 29, at the application rate of 0.4 L/ha (120 g clopyralid/ha).

One plot remained untreated.

Sampling was performed at 0 DBA (Days Before Application) on untreated plot and at 0 DAA (Days After Application) on the treated plot, then treated plot was sampled at BBCH 39, BBCH 59 and at BBCH 77. At BBCH 89 (at maturity of the crop) untreated and treated plots were sampled.

Clopyralid (Sum of Clopyralid, its salts and conjugates) residues were analysed in samples harvested during the field phase.

### Field phase description

The objective of the study was to determine the residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in Oilseed Rape raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The following pattern was designed for the treatments and the samplings:

#### 1.1.1.1 Application details

Plot	Test Item	App. No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	CHR/H/CPD 300 SL	T1	BBCH 29	0.4 L/ha	120 g/ha	200-300 L/ha (±10%)

#### 1.1.1.2 Sampling Details

##### Decline curve trial

Sampling event	Plot	Timing	Matrix	Min. Sample size
S1	U	0 DBA	Whole plants	0.1 kg, 12 plants
	T	0 DAA	Whole plants	0.1 kg, 12 plants
S2	T	BBCH 39	Whole plants	0.2 kg, 12 plants
S3	T	BBCH 59	Whole plants	0.5 kg, 12 plants
S4	T	BBCH 77	Ears	0.5 kg from 12 plants
			Rest of plants	1 kg from 12 plants
S5	U, T	BBCH 89	Grain	1 kg from 12 plants
			Straw	0.5 kg from 12 plants

DBA : Days before application

DAA : Days after application

### Location of the trial

The trial was performed on soil type and under cultural practices typical for oilseed rape production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Crop	Type of trial	European area	Region country
1	C2114 BW1	Audrey MEYER	Winter wheat	DC	North	Baden-Württemberg, Germany

DC: Decline curve



#### Identity and composition of the test item(s):

##### Test item

Trade or Code Name	CHR/H/CPD 300 SL
Active substance (a.s.)	Clopyralid
Formulation type	SL
CAS Number	[1702-17-6]
Nominal content of a.s.	300 g/L (expressed as clopyralid)
Batch number*	02/2018
Actual content *	30.18 %
Expiry date*	31/12/2022

#### General Information on the trial

##### Crop and soil Information

Trial No.	Crop	Variety	Crop density (seeds/m <sup>2</sup> )	Sowing / Planting date	Soil type	pH	Organic matter (%)
C2114 BW1	Winter wheat	PERKUSSIO	350	29/10/2021	Sandy Loam	7.6	2.3

#### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (cm)	Pressure (bars)
C2114 BW1	PULVEXPER	Flat fan	Teejet XR 110 015 VS	3	9	33	1.9

#### Summary of the actual application(s) data

Trial No.	Plot	Application No.	Active substance rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2114 BW1	T	1	118.7	-1.1	297	26/03/2022	29

#### Sampling of specimens

Trial No	Sampling	Actual Date	Actual DAA	Actual Growth Stage (BBCH)
C2114 BW1	1	26/03/2022	U : 0 DBA T : 0 DAA	29
	2	06/05/2022	41	39
	3	18/05/2022	53	59
	4	17/06/2022	83	77
	5	04/07/2022 + 05/07/2022*	100	89

DBA: Days before application

DAA: Days after application

\*Sampling in the field on 04/07/2022 and threshing on 05/07/2022.

#### ANALYTICAL PHASE

The objective of the analytical phase was to determine residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in raw agricultural commodity (RAC) specimens generated during the field phase.

#### Experimental details

##### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trial.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table::



#### TRIAL No. C2114 BW1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2114 01 01	C2114 BW1 / U0 / A	26/03/2022	05/04/2023	375	07/04/2023	2
C2114 01 02	C2114 BW1 / T0 / A	26/03/2022	06/04/2023	376	07/04/2023	1
C2114 01 03	C2114 BW1 / T39 / A	06/05/2022	06/04/2023	335	07/04/2023	1
C2114 01 04	C2114 BW1 / T59 / A	18/05/2022	06/04/2023	323	07/04/2023	1
C2114 01 05	C2114 BW1 / T77E / A	17/06/2022	26/04/2023	313	03/05/2023	7
C2114 01 06	C2114 BW1 / T77R / A	17/06/2022	19/04/2023	306	20/04/2023	1
C2114 01 07	C2114 BW1 / UHG / A	04/07/2022	27/04/2023	297	05/05/2023	8
C2114 01 08	C2114 BW1 / UHS / A	04/07/2022	28/04/2023	298	30/04/2023	2
C2114 01 09	C2114 BW1 / THG / A	04/07/2022	27/04/2023	297	05/05/2023	8
C2114 01 10	C2114 BW1 / THS / A	04/07/2022	28/04/2023	298	30/04/2023	2

\*Frozen storage time of samples from sampling to extraction (days)

\*\* Refrigerated storage time of final extracts, from extraction to analysis (days)

#### Storage stability of specimens

Specimens were stored frozen for no more than 376 days for whole plant, 306 days for rest of plants, 313 days for ears and 297 days for grain and 298 for straw from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in dry/high starch content commodities (straw) and for at least 13 months in whole plant, rest of plant, grain and ears (EFSA Journal Volume19, Issue1, January 2021, e06389).

#### Specimen preparation

The specimens were prepared according to ANADIAG SOPs.

The whole samples were individually blended with dry ice. A representative subspecimen was sampled after homogenization and placed for at least 12 hours at  $T < -18^{\circ}\text{C}$  for sublimation of dry ice. The subspecimen was kept frozen until an aliquot (2 g) was taken for analysis. A spare blended sample was also kept.

#### Specimen analysis

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

The applicability of the method in rest of plants and ears was demonstrated in the ANADIAG study C2103 entitled “Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Winter Wheat Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022”

Principle of the method

Residues of clopyralid and its conjugates were extracted and hydrolysed from samples by heating at  $60^{\circ}\text{C}$  for 3 hours with 2.5M KOH. After acidification with  $\text{H}_2\text{SO}_4$ , addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract was purified with a liquid-liquid partition. An aliquot of the upper layer was evaporated to dryness and the sample was reconstituted in 50:50, methanol/ $\text{H}_2\text{O}$  + 0.1% formic acid. Extracts were analysed by LC-MS/MS.

ANADIAG References (French version) of the method were

for the preparation and extraction of the samples: **SOP MP 718**

for the analysis of extracts and for the calibration: **SOP MA 1809**.

#### LOD

The limit of detection (LOD) was expressed as lowest calibration standard.

The LOD was 0.4 ng/mL for each matrix, corresponding to 0.002 mg/kg for clopyralid and 0.003

**mg/kg for clopyralid glycine.**

## **LOQ**

**The limit of quantification has been validated by fortifications at this level.**

**The LOQ was 0.01 mg/kg for each matrix and each analyte.**

## **Preparation of standard solutions**

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

	Solvent	Concentration	Storage conditions	Expiry date (Preparation + ...)
<b>Stock solution Clopyralid</b>	Acetonitrile	≈ 1 mg/mL	Frozen	6 months
<b>Stock solution Clopyralid glycine</b>	Methanol	≈ 1 mg/mL	Frozen	6 months
<b>Spiking solutions Clopyralid glycine</b>	Acetonitrile	≈ 0.2, 2, 20 or 200 µg/mL	Frozen	1 month
<b>Intermediate calibration solutions Clopyralid</b>	Control extract	≈ 200 and 20 ng/mL	Refrigerated	14 days
<b>Matrix-matched Calibration solutions Clopyralid</b>	Control extract	≈ 0.4 to 24 ng/mL	Refrigerated	14 days

## **Calibration curves**

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas obtained from chromatograms were plotted versus concentrations and the calibration functions were determined by least square fit.

Number and concentrations of standards used (min. 5 calibration levels), as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve (r) must be ≥ 0.990 for the calibration to be acceptable.

All extracts analysed (after dilution when required) fell within the range of the standard curve.

## **Fortification procedure**

Fortifications were performed by adding known amounts of the spiking solutions of clopyralid glycine to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

The recoveries of the spiked samples met with the acceptance criteria described in SANTE/2020/12830, Rev.1.

#### Blank Samples:

Analytical sample No.	Matrix	Clopyralid residues found (mg/kg)	Clopyralid glycine residues found (mg/kg)
S616 01 11	Whole plants	NDR	NDR
S607 01 11	Ears	NDR	NDR
S606 01 31	Rest of plants	NDR	NDR
S617 01 11	Grain	NDR	NDR
S618 01 11	Straw	NDR	NDR

#### Spiked samples:

Analytical Sample No.	Matrix	Fortification level (mg/kg)	% Recovery*	Extraction date	Storage time of extracts**	Spiked with
S616 01 AA	Whole plants	0.01	93.5%	05/04/2023	2	Clopyralid glycine
S616 01 BA D100		10	85.0%	06/04/2023	1	
S616 01 CB D200		20	73.0%	13/04/2023	6	
S607 01 AA	Ears	0.01	73.6%	26/04/2023	6	
S607 01 BA D10		1.0	93.2%	26/04/2023	7	
S607 01 CA d100		10	90.4%	09/05/2023	1	
S606 01 EA	Rest of plants	0.01	78.7%	28/04/2023	1	
S606 01 DA D10		0.99	71.5%	19/04/2023	1	
S617 01 CA	Grain	0.01	89.3%	16/05/2023	0	
S617 01 BA D10		1.0	75.1%	27/04/2023	8	
S618 01 AA	Straw	0.01	76.6%	28/04/2023	2	
S618 01 BA D10		1.0	84.0%	02/05/2023	3	

\*Amount in control subtracted if above LOD.

\*\*Refrigerated storage time of final extracts, from extraction to analysis (days)

## Results

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2114 BW1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2114 01 01	C2114 BW1 / U0 / A	-	Whole plants	-	NDR
C2114 01 02	C2114 BW1 / T0 / A	CHR/H/CPD 300 SL	Whole plants	0	11.15
C2114 01 03	C2114 BW1 / T39 / A	CHR/H/CPD 300 SL	Whole plants	41	1.05
C2114 01 04	C2114 BW1 / T59 / A	CHR/H/CPD 300 SL	Whole plants	53	0.40
C2114 01 05	C2114 BW1 / T77E / A	CHR/H/CPD 300 SL	Ears	83	0.69
C2114 01 06	C2114 BW1 / T77R / A	CHR/H/CPD 300 SL	Rest of plants	83	0.44
C2114 01 07	C2114 BW1 / UHG / A	-	Grain	-	NDR
C2114 01 08	C2114 BW1 / UHS / A	-	Straw	-	NDR
C2114 01 09	C2114 BW1 / THG / A	CHR/H/CPD 300 SL	Grain	100	0.45
C2114 01 10	C2114 BW1 / THS / A	CHR/H/CPD 300 SL	Straw	100	0.52

DAA: Days after application

NDR: No detectable residues (residues below the limit of detection)

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

#### A 2.1.3.1.1.19 Study 19

Reference:	KCA 6.3/19
Report	Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Winter Wheat Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022, E. Schneider, 2023, C2115, Anadiag, France
Guideline(s):	Regulation (EC) No. 1107/2009 Regulation (EU) No. 283/2013 and 284/2013 2004/10/EC GLP Directive OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021 SANTE/2019/12752 - Technical guidelines on data requirements for setting Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin. SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.
Deviations:	<b>Deviation No. 03/06/2022</b> Trial C2115 PL1: At sampling No.3 (BBCH 59), the whole plants (no roots) were cut at 15 cm above soil level instead of at soil level as required by the study plan. According to the study plan, it is only allowed to cut plants at 15 cm above the soil after BBCH 59. The deviation was due to an error of the principal investigator. The deviation has no impact on the study as it concerns a sampling at an immature growth stage of the crop and as the final plant height was already reached. <b>Deviation No. 12/07/2022</b> Trial C2115 PL1: At sampling No.4, the growth stage was BBCH 77-83 instead of BBCH 77 as required by the study plan. 50% of the plants were at BBCH 77 and 50% of plants were at BBCH 83. The crop development was faster than scheduled. The deviation has no impact on the study as 50% of the plants were at the required growth stage and as it is an immature growth stage.
GLP:	Yes
Acceptability:	Yes

#### Objective of the study

The objective of the study was to determine the residue levels of Clopyralid (Sum of Clopyralid, its salts and conjugates) in Winter wheat raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at 1 site in Northern Europe. The trial was sampled frequently to monitor the decline of residues shortly after the treatment.

One plot was treated once with CHR/H/CPD 300 SL at BBCH 29, at the application rate of 0.4 L/ha (120 g clopyralid/ha).

One plot remained untreated.

Sampling was performed at 0 DBA (Day Before application) on untreated plot and at 0 DAA (Days After Application) on the treated plot, then treated plot was sampled at BBCH 39, BBCH 59 and at BBCH 77-

83 (see deviation No. 12/07/2022). At BBCH 89 (at maturity of the crop) untreated and treated plots were sampled.

Clopyralid (Sum of Clopyralid, its salts and conjugates) residues were analysed in samples harvested during the field phase.

### Field phase description

The objective of the study was to determine the residue levels of Clopyralid (Sum of Clopyralid, its salts and conjugates) in Winter wheat raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The following pattern was designed for the treatments and the samplings:

#### 1.1.1.1 Application details

Plot	Test Item	App. No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	CHR/H/CPD 300 SL	T1	BBCH 29	0.4 L/ha	120 g/ha	200-300 L/ha (±10%)

#### 1.1.1.2 Sampling Details

##### Decline curve trial

Sampling event	Plot	Timing	Matrix	Min. Sample size
S1	U	0 DBA	Whole plants	0.1 kg, 12 plants
	T	0 DAA	Whole plants	0.1 kg, 12 plants
S2	T	BBCH 39	Whole plants	0.2 kg, 12 plants
S3	T	BBCH 59	Whole plants	0.5 kg, 12 plants
S4	T	BBCH 77	Ears	0.5 kg from 12 plants
			Rest of plants	1 kg from 12 plants
S5	U, T	BBCH 89	Grain	1 kg from 12 plants
			Straw	0.5 kg from 12 plants

DBA : Days before application

DAA : Days after application

### Location of the trial

The trial was performed on soil type and under cultural practices typical for oilseed rape production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Crop	Type of trial	European area	Region country
1	C2115 PL1	Krzysztof NOWAK	Winter wheat	DC	North	Lodzkie, Poland

DC: Decline curve

## Localisation



### Identity and composition of the test item(s):

#### Test item

Trade or Code Name	CHR/H/CPD 300 SL
Active substance (a.s.)	Clopyralid
Formulation type	SL
CAS Number	[1702-17-6]
Nominal content of a.s.	300 g/L (expressed as clopyralid)
Batch number*	02/2018
Actual content *	30.18 %
Expiry date*	31/12/2022

### General Information on the trial

#### Crop and soil Information

Trial No.	Crop	Variety	Crop density (kg/ha)	Sowing / Planting date	Soil type	pH	Organic matter (%)
C2115 PL1	Winter wheat	Belissa	220	08/10/2021	Loamy Sand	6.5	1.5

#### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (cm)	Pressure (bars)
C2115 PL1	Europulve	Flat fan	Teejet XR 110 02 VS	3	9	33.33	3.0

#### Summary of the actual application(s) data

Trial No.	Plot	Application No.	Active substance rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2115 PL1	T	1	115.7	-3.6	289	29/04/2022	29

#### Sampling of specimens

Trial No	Sampling	Actual Date	Actual DAA	Actual Growth Stage (BBCH)
C2115 PL1	1	29/04/2022	U : 0 DBA T : 0 DAA	29
	2	20/05/2022	21	39
	3	03/06/2022	35	59
	4	07/07/2022	69	77-83*
	5	21/07/2022	83	89

DBA: Days before application

DAA: Days after application

\*See deviation No. 12/07/2022

#### ANALYTICAL PHASE

The objective of the analytical phase was to determine residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in raw agricultural commodity (RAC) specimens generated during the field phase.

#### Experimental details

##### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trial.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table::



### TRIAL No. C2115 PL1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2115 01 01	C2115 PL1 / U0 / A	29/04/2022	06/04/2023	342	07/04/2023	1
C2115 01 02	C2115 PL1 / T0 / A	29/04/2022	05/04/2023	341	07/04/2023	2
C2115 01 03	C2115 PL1 / T39 / A	20/05/2022	05/04/2023	320	07/04/2023	2
C2115 01 04	C2115 PL1 / T59 / A	03/06/2022	05/04/2023	306	07/04/2023	2
C2115 01 05	C2115 PL1 / T77E / A	07/07/2022	26/04/2023	293	03/05/2023	7
C2115 01 06	C2115 PL1 / T77R / A	07/07/2022	19/04/2023	286	20/04/2023	1
C2115 01 07	C2115 PL1 / UHG / A	21/07/2022	27/04/2023	280	05/05/2023	8
C2115 01 08	C2115 PL1 / UHS / A	21/07/2022	02/05/2023	285	05/05/2023	3
C2115 01 09	C2115 PL1 / THG / A	21/07/2022	27/04/2023	280	05/05/2023	8
C2115 01 10	C2115 PL1 / THS / A	21/07/2022	02/05/2023	285	05/05/2023	3

\*Frozen storage time of samples from sampling to extraction (days)

\*\* Refrigerated storage time of final extracts, from extraction to analysis (days)

### Storage stability of specimens

Specimens were stored frozen for no more than 342 days for whole plant, 286 days for rest of plants, 293 days for ears and 280 days for grain and 285 for straw from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in dry/high starch content commodities (straw) and for at least 13 months in whole plant, rest of plant, grain and ears (EFSA Journal Volume19, Issue1, January 2021, e06389).

### Specimen preparation

The specimens were prepared according to ANADIAG SOPs.

The whole samples were individually blended with dry ice. A representative subspecimen was sampled after homogenization and placed for at least 12 hours at T < -18°C for sublimation of dry ice. The subspecimen was kept frozen until an aliquot (2 g) was taken for analysis. A spare blended sample was also kept.

### Specimen analysis

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

The applicability of the method in rest of plants and ears was demonstrated in the ANADIAG study C2103 entitled “Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Winter Wheat Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022”

Principle of the method

Residues of clopyralid and its conjugates were extracted and hydrolysed from samples by heating at 60 °C for 3 hours with 2.5M KOH. After acidification with H<sub>2</sub>SO<sub>4</sub>, addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract was purified with a liquid-liquid partition. An aliquot of the upper layer was evaporated to dryness and the sample was reconstituted in 50:50, methanol/H<sub>2</sub>O + 0.1% formic acid. Extracts were analysed by LC-MS/MS.

ANADIAG References (French version) of the method were

for the preparation and extraction of the samples: **SOP MP 718**

for the analysis of extracts and for the calibration: **SOP MA 1809**.

### LOD

The limit of detection (LOD) was expressed as lowest calibration standard.

The LOD was 0.4 ng/mL for each matrix, corresponding to 0.002 mg/kg for clopyralid and 0.003

**mg/kg for clopyralid glycine.**

#### **LOQ**

**The limit of quantification has been validated by fortifications at this level.**

**The LOQ was 0.01 mg/kg for each matrix and each analyte.**

#### **Preparation of standard solutions**

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item..

	<b>Solvent</b>	<b>Concentration</b>	<b>Storage conditions</b>	<b>Expiry date (Preparation + ...)</b>
<b>Stock solution Clopyralid</b>	Acetonitrile	≈ 1 mg/mL	Frozen	6 months
<b>Stock solution Clopyralid glycine</b>	Methanol	≈ 1 mg/mL	Frozen	6 months
<b>Spiking solutions Clopyralid glycine</b>	Acetonitrile	≈ 0.2, 2, 20 or 200 µg/mL	Frozen	1 month
<b>Intermediate calibration solutions Clopyralid</b>	Control extract	≈ 200 and 20 ng/mL	Refrigerated	14 days
<b>Matrix-matched Calibration solutions Clopyralid</b>	Control extract	≈ 0.4 to 24 ng/mL	Refrigerated	14 days

#### **Calibration curves**

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas obtained from chromatograms were plotted versus concentrations and the calibration functions were determined by least square fit.

Number and concentrations of standards used (min. 5 calibration levels), as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve (r) must be  $\geq 0.990$  for the calibration to be acceptable.

All extracts analysed (after dilution when required) fell within the range of the standard curve.

#### **Fortification procedure**

Fortifications were performed by adding known amounts of the spiking solutions of clopyralid glycine to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

#### Blank Samples:

Analytical sample No.	Matrix	Clopyralid residues found (mg/kg)	Clopyralid glycine residues found (mg/kg)
S616 01 11	Whole plants	NDR	NDR
S607 01 11	Ears	NDR	NDR
S606 01 31	Rest of plants	NDR	NDR
S617 01 11	Grain	NDR	NDR
S618 01 11	Straw	NDR	NDR

#### Spiked samples:

Analytical Sample No.	Matrix	Fortification level (mg/kg)	% Recovery*	Extraction date	Storage time of extracts**	Spiked with
S616 01 AA	Whole plants	0.01	93.5%	05/04/2023	2	Clopyralid glycine
S616 01 BA D100		10	85.0%	06/04/2023	1	
S616 01 CB D200		20	73.0%	13/04/2023	6	
S607 01 AA	Ears	0.01	73.6%	26/04/2023	6	
S607 01 BA D10		1.0	93.2%	26/04/2023	7	
S607 01 CA d100		10	90.4%	09/05/2023	1	
S606 01 EA	Rest of plants	0.01	78.7%	28/04/2023	1	
S606 01 DA D10		0.99	71.5%	19/04/2023	1	
S617 01 CA	Grain	0.01	89.3%	16/05/2023	0	
S617 01 BA D10		1.0	75.1%	27/04/2023	8	
S618 01 AA	Straw	0.01	76.6%	28/04/2023	2	
S618 01 BA D10		1.0	84.0%	02/05/2023	3	

\*Amount in control subtracted if above LOD.

\*\*Refrigerated storage time of final extracts, from extraction to analysis (days)

## Results

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2115 PL1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2115 01 01	C2115 PL1 / U0 / A	-	Whole plants	-	NDR
C2115 01 02	C2115 PL1 / T0 / A	CHR/H/CPD 300 SL	Whole plants	0	4.11
C2115 01 03	C2115 PL1 / T39 / A	CHR/H/CPD 300 SL	Whole plants	21	0.70
C2115 01 04	C2115 PL1 / T59 / A	CHR/H/CPD 300 SL	Whole plants	35	1.05
C2115 01 05	C2115 PL1 / T77E / A	CHR/H/CPD 300 SL	Ears	69	1.87
C2115 01 06	C2115 PL1 / T77R / A	CHR/H/CPD 300 SL	Rest of plants	69	0.54
C2115 01 07	C2115 PL1 / UHG / A	-	Grain	-	NDR
C2115 01 08	C2115 PL1 / UHS / A	-	Straw	-	NDR
C2115 01 09	C2115 PL1 / THG / A	CHR/H/CPD 300 SL	Grain	83	0.80
C2115 01 10	C2115 PL1 / THS / A	CHR/H/CPD 300 SL	Straw	83	0.81

DAA: Days after application

NDR: No detectable residues (residues below the limit of detection)

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

#### A 2.1.3.1.1.20 Study 20

Reference:	KCA 6.3/20
Report	Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Winter Wheat Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022, E. Schneider, 2023, C2116, Anadiag, France
Guideline(s):	Regulation (EC) No. 1107/2009 Regulation (EU) No. 283/2013 and 284/2013 2004/10/EC GLP Directive OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021 SANTE/2019/12752 - Technical guidelines on data requirements for setting Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin. SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.
Deviations:	No
GLP:	Yes
Acceptability:	Yes

#### Objective of the study

The objective of the study was to determine the residue levels of Clopyralid (Sum of Clopyralid, its salts and conjugates) in Winter wheat raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at 1 site in Northern Europe. The trial was sampled frequently to monitor the decline of residues shortly after the treatment.

One plot was treated once with CHR/H/CPD 300 SL at BBCH 29, at the application rate of 0.4 L/ha (120 g clopyralid/ha).

One plot remained untreated.

Sampling was performed at 0 DBA (Day Before application) on untreated plot and at 0 DAA (Days After Application) on the treated plot, then treated plot was sampled at BBCH 39, BBCH 59 and at BBCH 77.

At BBCH 89 (at maturity of the crop) untreated and treated plots were sampled.

Clopyralid (Sum of Clopyralid, its salts and conjugates) residues were analysed in samples harvested during the field phase.

#### Field phase description

The objective of the study was to determine the residue levels of Clopyralid (Sum of Clopyralid, its salts and conjugates) in Winter wheat raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The following pattern was designed for the treatments and the samplings:

#### 1.1.1.1 Application details

Plot	Test Item	App. No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	CHR/H/CPD 300 SL	T1	BBCH 29	0.4 L/ha	120 g/ha	200-300 L/ha (±10%)

#### 1.1.1.2 Sampling Details

##### Decline curve trial

Sampling event	Plot	Timing	Matrix	Min. Sample size
S1	U	0 DBA	Whole plants	0.1 kg, 12 plants
	T	0 DAA	Whole plants	0.1 kg, 12 plants
S2	T	BBCH 39	Whole plants	0.2 kg, 12 plants
S3	T	BBCH 59	Whole plants	0.5 kg, 12 plants
S4	T	BBCH 77	Ears	0.5 kg from 12 plants
			Rest of plants	1 kg from 12 plants
S5	U, T	BBCH 89	Grain	1 kg from 12 plants
			Straw	0.5 kg from 12 plants

DBA : Days before application  
DAA : Days after application

#### Location of the trial

The trial was performed on soil type and under cultural practices typical for oilseed rape production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Crop	Type of trial	European area	Region country
1	C2116 CZ1	Iva SIMEK	Winter wheat	DC	North	Pardubicky, Czech Republic

DC: Decline curve

## Localisation



### Identity and composition of the test item(s):

#### Test item

Trade or Code Name	CHR/H/CPD 300 SL
Active substance (a.s.)	Clopyralid
Formulation type	SL
CAS Number	[1702-17-6]
Nominal content of a.s.	300 g/L (expressed as clopyralid)
Batch number*	02/2018
Actual content *	30.18 %
Expiry date*	31/12/2022

### General Information on the trial

#### Crop and soil Information

Trial No.	Crop	Variety	Crop density (kg/ha)	Sowing / Planting date	Soil type	pH	Organic matter (%)
C2116 CZ1	Winter wheat	REGISTANA	200	12/10/2021	Sandy Clay Loam	5.3	1.8

#### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (cm)	Pressure (bars)
C2116 CZ1	Pulvexper	Flat fan	Teejet XR 110 015 VS	3	9	33	2

#### Summary of the actual application(s) data

Trial No.	Plot	Application No.	Active substance rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2116 CZ1	T	1	118.4	-1.3	247	20/04/2022	29

#### Sampling of specimens

##### Sampling summary

Trial No	Sampling	Actual Date	Actual DAA	Actual Growth Stage (BBCH)
C2116 CZ1	1	20/04/2022	U : 0 DBA T : 0 DAA	29
	2	10/05/2022	20	39
	3	22/05/2022	32	59
	4	16/06/2022	57	77
	5	12/07/2022	83	89

DBA: Days before application

DAA: Days after application

#### ANALYTICAL PHASE

The objective of the analytical phase was to determine residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in raw agricultural commodity (RAC) specimens generated during the field phase.

#### Experimental details

##### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trial.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table::



#### TRIAL No. C2116 CZ1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2116 01 01	C2116 CZ1 / U0 / A	20/04/2022	05/04/2023	350	07/04/2023	2
C2116 01 02	C2116 CZ1 / T0 / A	20/04/2022	05/04/2023	350	07/04/2023	2
C2116 01 03	C2116 CZ1 / T39 / A	10/05/2022	05/04/2023	330	19/04/2023	14
C2116 01 04	C2116 CZ1 / T59 / A	22/05/2022	05/04/2023	318	07/04/2023	2
C2116 01 05	C2116 CZ1 / T77E / A	16/06/2022	26/04/2023	314	03/05/2023	7
C2116 01 06	C2116 CZ1 / T77R / A	16/06/2022	19/04/2023	307	20/04/2023	1
C2116 01 07	C2116 CZ1 / UHG / A	12/07/2022	27/04/2023	289	05/05/2023	8
C2116 01 08	C2116 CZ1 / UHS / A	12/07/2022	28/04/2023	290	30/04/2023	2
C2116 01 09	C2116 CZ1 / THG / A	12/07/2022	27/04/2023	289	05/05/2023	8
C2116 01 10	C2116 CZ1 / THS / A	12/07/2022	28/04/2023	290	30/04/2023	2

\*Frozen storage time of samples from sampling to extraction (days)

\*\* Refrigerated storage time of final extracts, from extraction to analysis (days)

#### Storage stability of specimens

Specimens were stored frozen for no more than 350 days for whole plant, 307 days for rest of plants, 314 days for ears and 289 days for grain and 290 for straw from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in dry/high starch content commodities (straw) and for at least 13 months in whole plant, rest of plant, grain and ears (EFSA Journal Volume19, Issue1, January 2021, e06389).

#### Specimen preparation

The specimens were prepared according to ANADIAG SOPs.

The whole samples were individually blended with dry ice. A representative subspecimen was sampled after homogenization and placed for at least 12 hours at T < -18°C for sublimation of dry ice. The subspecimen was kept frozen until an aliquot (2 g) was taken for analysis. A spare blended sample was also be kept.

#### Specimen analysis

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

The applicability of the method in rest of plants and ears was demonstrated in the ANADIAG study C2103 entitled “Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Winter Wheat Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022”

Principle of the method

Residues of clopyralid and its conjugates were extracted and hydrolysed from samples by heating at 60 °C for 3 hours with 2.5M KOH. After acidification with H<sub>2</sub>SO<sub>4</sub>, addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract was purified with a liquid-liquid partition. An aliquot of the upper layer was evaporated to dryness and the sample was reconstituted in 50:50, methanol/H<sub>2</sub>O + 0.1% formic acid. Extracts were analysed by LC-MS/MS.

ANADIAG References (French version) of the method were

for the preparation and extraction of the samples: **SOP MP 718**

for the analysis of extracts and for the calibration: **SOP MA 1809**

#### LOD

The limit of detection (LOD) was expressed as lowest calibration standard.

The LOD was 0.4 ng/mL for each matrix, corresponding to 0.002 mg/kg for clopyralid and 0.003

**mg/kg for clopyralid glycine.**

#### **LOQ**

**The limit of quantification has been validated by fortifications at this level.**

**The LOQ was 0.01 mg/kg for each matrix and each analyte.**

#### **Preparation of standard solutions**

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item..

	<b>Solvent</b>	<b>Concentration</b>	<b>Storage conditions</b>	<b>Expiry date (Preparation + ...)</b>
<b>Stock solution Clopyralid</b>	Acetonitrile	≈ 1 mg/mL	Frozen	6 months
<b>Stock solution Clopyralid glycine</b>	Methanol	≈ 1 mg/mL	Frozen	6 months
<b>Spiking solutions Clopyralid glycine</b>	Acetonitrile	≈ 0.2, 2, 20 or 200 µg/mL	Frozen	1 month
<b>Intermediate calibration solutions Clopyralid</b>	Control extract	≈ 200 and 20 ng/mL	Refrigerated	14 days
<b>Matrix-matched Calibration solutions Clopyralid</b>	Control extract	≈ 0.4 to 24 ng/mL	Refrigerated	14 days

#### **Calibration curves**

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas obtained from chromatograms were plotted versus concentrations and the calibration functions were determined by least square fit.

Number and concentrations of standards used (min. 5 calibration levels), as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve (r) must be  $\geq 0.990$  for the calibration to be acceptable.

All extracts analysed (after dilution when required) fell within the range of the standard curve.

#### **Fortification procedure**

Fortifications were performed by adding known amounts of the spiking solutions of clopyralid glycine to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

#### Blank Samples:

Analytical sample No.	Matrix	Clopyralid residues found (mg/kg)	Clopyralid glycine residues found (mg/kg)
S616 01 11	Whole plants	NDR	NDR
S607 01 11	Ears	NDR	NDR
S606 01 31	Rest of plants	NDR	NDR
S617 01 11	Grain	NDR	NDR
S618 01 11	Straw	NDR	NDR

deviation

2/2 <

#### Spiked samples:

Analytical Sample No.	Matrix	Fortification level (mg/kg)	% Recovery*	Extraction date	Storage time of extracts**	Spiked with
S616 01 AA	Whole plants	0.01	93.5%	05/04/2023	2	Clopyralid glycine
S616 01 BA D100		10	85.0%	06/04/2023	1	
S616 01 CB D200		20	73.0%	13/04/2023	6	
S607 01 AA	Ears	0.01	73.6%	26/04/2023	6	
S607 01 BA D10		1.0	93.2%	26/04/2023	7	
S607 01 CA d100		10	90.4%	09/05/2023	1	
S606 01 EA	Rest of plants	0.01	78.7%	28/04/2023	1	
S606 01 DA D10		0.99	71.5%	19/04/2023	1	
S617 01 CA	Grain	0.01	89.3%	16/05/2023	0	
S617 01 BA D10		1.0	75.1%	27/04/2023	8	
S618 01 AA	Straw	0.01	76.6%	28/04/2023	2	
S618 01 BA D10		1.0	84.0%	02/05/2023	3	

\*Amount in control subtracted if above LOD.

\*\*Refrigerated storage time of final extracts, from extraction to analysis (days)

## Results

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2116 CZ1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2116 01 01	C2116 CZ1 / U0 / A	-	Whole plants	-	< LOQ
C2116 01 02	C2116 CZ1 / T0 / A	CHR/H/CPD 300 SL	Whole plants	0	5.55
C2116 01 03	C2116 CZ1 / T39 / A	CHR/H/CPD 300 SL	Whole plants	20	2.59
C2116 01 04	C2116 CZ1 / T59 / A	CHR/H/CPD 300 SL	Whole plants	32	1.64
C2116 01 05	C2116 CZ1 / T77E / A	CHR/H/CPD 300 SL	Ears	57	2.52
C2116 01 06	C2116 CZ1 / T77R / A	CHR/H/CPD 300 SL	Rest of plants	57	0.79
C2116 01 07	C2116 CZ1 / UHG / A	-	Grain	-	NDR
C2116 01 08	C2116 CZ1 / UHS / A	-	Straw	-	NDR
C2116 01 09	C2116 CZ1 / THG / A	CHR/H/CPD 300 SL	Grain	83	0.54
C2116 01 10	C2116 CZ1 / THS / A	CHR/H/CPD 300 SL	Straw	83	0.76

DAA: Days after application

NDR: No detectable residues (residues below the limit of detection)

< LOQ: residues between LOD and LOQ

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

#### A 2.1.3.1.1.21 Study 21

Reference:	KCA 6.3/21
Report	Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Winter Wheat Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022, E. Schneider, 2023, C2117, Anadiag, France
Guideline(s):	Regulation (EC) No. 1107/2009 Regulation (EU) No. 283/2013 and 284/2013 2004/10/EC GLP Directive OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021 SANTE/2019/12752 - Technical guidelines on data requirements for setting Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin. SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.
Deviations:	No
GLP:	Yes
Acceptability:	Yes

#### Objective of the study

The objective of the study was to determine the residue levels of Clopyralid (Sum of Clopyralid, its salts and conjugates) in Winter wheat raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at 1 site in Northern Europe. The trial was sampled at harvest.

One plot was treated once with CHR/H/CPD 300 SL at BBCH 29, at the application rate of 0.4 L/ha (120 g clopyralid/ha).

One plot remained untreated.

Sampling was performed at BBCH 89 (at maturity of the crop) in untreated and treated plots.

Clopyralid (Sum of Clopyralid, its salts and conjugates) residues were analysed in samples harvested during the field phase.

#### Field phase description

The objective of the study was to determine the residue levels of Clopyralid (Sum of Clopyralid, its salts and conjugates) in Winter wheat raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The following pattern was designed for the treatments and the samplings:

#### 1.1.1.1 Application details

Plot	Test Item	App. No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	CHR/H/CPD 300 SL	T1	BBCH 29	0.4 L/ha	120 g/ha	200-300 L/ha (±10%)

#### 1.1.1.2 Sampling Details

##### Residue at Harvest

Sampling event	Plot	Timing	Matrix	Min. Sample size
S1	U, T	BBCH 89	Grain	1 kg from 12 plants
			Straw	0.5 kg from 12 plants

#### Location of the trial

The trial was performed on soil type and under cultural practices typical for oilseed rape production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Crop	Type of trial	European area	Region country
1	C2117 MA1	Benoît BOYETTE	Winter wheat	RH	North	Grand-Est, France

RH: Residue at Harvest

## Localisation



## Identity and composition of the test item(s):

### Test item

Trade or Code Name	CHR/H/CPD 300 SL
Active substance (a.s.)	Clopyralid
Formulation type	SL
CAS Number	[1702-17-6]
Nominal content of a.s.	300 g/L (expressed as clopyralid)
Batch number*	02/2018
Actual content *	30.18 %
Expiry date*	31/12/2022

## General Information on the trial

### Crop and soil Information

Trial No.	Crop	Variety	Crop density (kg/ha)	Sowing / Planting date	Soil type	pH	Organic matter (%)
C2117 MA1	Winter wheat	CHEVIGNON	160	28/09/2021	Clay	8	3

## Application equipment

Hand boom sprayer was used with the following conditions:

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (cm)	Pressure (bars)
C2117 MA1	AGRISER	Flat fan	Teejet XR 110 015 VS	3	9	33	2

#### Summary of the actual application(s) data

Trial No.	Plot	Application No.	Active substance rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2117 MA1	T	1	122.7	+2.2	307	27/03/2022	29

#### Sampling of specimens

Trial No	Sampling	Actual Date	Actual DAA	Actual Growth Stage (BBCH)
C2117 MA1	1	12/07/2022	107	89

DAA: Days after application

#### ANALYTICAL PHASE

The objective of the analytical phase was to determine residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in raw agricultural commodity (RAC) specimens generated during the field phase.

#### Experimental details

##### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trial.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table::

##### TRIAL No. C2117 MA1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2117 01 01	C2117 MA1 / UHG / A	12/07/2022	27/04/2023	289	05/05/2023	8
C2117 01 02	C2117 MA1 / UHS / A	12/07/2022	02/05/2023	294	05/05/2023	3
C2117 01 03	C2117 MA1 / THG / A	12/07/2022	27/04/2023	289	05/05/2023	8
C2117 01 04	C2117 MA1 / THS / A	12/07/2022	02/05/2023	294	05/05/2023	3

\*Frozen storage time of samples from sampling to extraction (days)

\*\* Refrigerated storage time of final extracts, from extraction to analysis (days)

#### Storage stability of specimens

Specimens were stored frozen for no more than 289 days for grain and 294 days for straw from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in dry/high starch content commodities (straw) and for at least 13 months in grain (EFSA Journal Volume19, Issue1, January 2021, e06389).

#### Specimen preparation

The specimens were prepared according to ANADIAG SOPs.

The whole samples were individually blended with dry ice. A representative subspecimen was sampled after homogenization and placed for at least 12 hours at T < -18°C for sublimation of dry ice. The subspecimen was kept frozen until an aliquot (2 g) was taken for analysis. A spare blended sample was also



be kept.

### Specimen analysis

Samples were analysed according to the method developed by ANADIAG and validated under ANADI-AG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

Principle of the method

Residues of clopyralid and its conjugates were extracted and hydrolysed from samples by heating at 60 °C for 3 hours with 2.5M KOH. After acidification with H<sub>2</sub>SO<sub>4</sub>, addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract was purified with a liquid-liquid partition. An aliquot of the upper layer was evaporated to dryness and the sample was reconstituted in 50:50, methanol/H<sub>2</sub>O + 0.1% formic acid. Extracts were analysed by LC-MS/MS.

ANADIAG References (French version) of the method were

for the preparation and extraction of the samples: **SOP MP 718**

for the analysis of extracts and for the calibration: **SOP MA 1809**

### LOD

The limit of detection (LOD) was expressed as lowest calibration standard.

The LOD was 0.4 ng/mL for each matrix, corresponding to 0.002 mg/kg for clopyralid and 0.003 mg/kg for clopyralid glycine.

### LOQ

The limit of quantification has been validated by fortifications at this level.

The LOQ was 0.01 mg/kg for each matrix and each analyte.

### Preparation of standard solutions

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

	Solvent	Concentration	Storage conditions	Expiry date (Preparation + ...)
Stock solution Clopyralid	Acetonitrile	≈ 1 mg/mL	Frozen	6 months
Stock solution Clopyralid glycine	Methanol	≈ 1 mg/mL	Frozen	6 months
Spiking solutions Clopyralid glycine	Acetonitrile	≈ 0.2 and 20 µg/mL	Frozen	1 month
Intermediate calibration solutions Clopyralid	Control extract	≈ 200 and 20 ng/mL	Refrigerated	14 days
Matrix-matched Calibration solutions Clopyralid	Control extract	≈ 0.4 to 24 ng/mL	Refrigerated	14 days

### Calibration curves

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas obtained from chromatograms were plotted versus concentrations and the calibration functions were determined by least square fit.

Number and concentrations of standards used (min. 5 calibration levels), as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve (r) must be ≥ 0.990 for the calibration to be acceptable.

All extracts analysed (after dilution when required) fell within the range of the standard curve.

### Fortification procedure

Fortifications were performed by adding known amounts of the spiking solutions of clopyralid glycine to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

**Blank Samples:**

Analytical sample No.	Matrix	Clopyralid residues found (mg/kg)	Clopyralid glycine residues found (mg/kg)
S617 01 11	Grain	NDR	NDR
S618 01 11	Straw	NDR	NDR

**Spiked samples:**

Analytical Sample No.	Matrix	Fortification level (mg/kg)	% Recovery*	Extraction date	Storage time of extracts**	Spiked with
S617 01 CA	Grain	0.01	89.3%	16/05/2023	0	Clopyralid glycine
S617 01 BA D10		1.0	75.1%	27/04/2023	8	
S618 01 AA	Straw	0.01	76.6%	28/04/2023	2	
S618 01 BA D10		1.0	84.0%	02/05/2023	3	

\*Amount in control subtracted if above LOD.

\*\*Refrigerated storage time of final extracts, from extraction to analysis (days)

**Results**

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2117 MA1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2117 01 01	C2117 MA1 / UHG / A	-	Grain	-	NDR
C2117 01 02	C2117 MA1 / UHS / A	-	Straw	-	NDR
C2117 01 03	C2117 MA1 / THG / A	CHR/H/CPD 300 SL	Grain	107	0.27
C2117 01 04	C2117 MA1 / THS / A	CHR/H/CPD 300 SL	Straw	107	0.59

DAA: Days after application

NDR: No detectable residues (residues below the limit of detection)

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

**A 2.1.3.1.1.22 Study 22**

Reference:	KCA 6.3/22
Report	Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Winter Wheat Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022, E. Schneider, 2023, C2103, Anadiag, France
Guideline(s):	Regulation (EC) No. 1107/2009 Regulation (EU) No. 283/2013 and 284/2013 2004/10/EC GLP Directive OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021 SANTE/2019/12752 - Technical guidelines on data requirements for setting Maximum Residue Levels, comparability of residue trials and extrapolation

of residue data on products from plant and animal origin.  
SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes  
OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.

Deviations:	No
GLP:	Yes
Acceptability:	Yes

#### Objective of the study

The objective of the study was to determine the residue levels of Clopyralid (Sum of Clopyralid, its salts and conjugates) in Winter wheat raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at 1 site in Northern Europe. The trial was sampled frequently to monitor the decline of residues shortly after the treatment.

One plot was treated once with CHR/H/CPD 300 SL at BBCH 29, at the application rate of 0.4 L/ha (120 g clopyralid/ha).

One plot remained untreated.

Sampling was performed at 0 DBA (Day Before application) on untreated plot and at 0 DAA (Days After Application) on the treated plot, then treated plot was sampled at BBCH 39, BBCH 59 and at BBCH 77. At BBCH 89 (at maturity of the crop) untreated and treated plots were sampled.

Clopyralid (Sum of Clopyralid, its salts and conjugates) residues were analysed in samples harvested during the field phase.

#### Field phase description

The objective of the study was to determine the residue levels of Clopyralid (Sum of Clopyralid, its salts and conjugates) in Winter wheat raw agricultural commodity (RAC) after one foliar application of the formulated product CHR/H/CPD 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

#### 1.1.1.1 Application details

Plot	Test Item(s)	Application No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	CHR/H/CPD 300 SL	T1	BBCH 29	0.4 L/ha	120 g/ha	200-300 L/ha (±10%)

#### 1.1.1.2 Sampling Details

Sampling event	Plot	Timing	Matrix	Min. Sample size
S1	U	0 DBA	Whole plants	0.1 kg, 12 plants
	T	0 DAA	Whole plants	0.1 kg, 12 plants
S2	T	BBCH 39	Whole plants	0.2 kg, 12 plants
S3	T	BBCH 59	Whole plants	0.5 kg, 12 plants
S4	T	BBCH 77	Ears	0.5 kg from 12 plants
			Rest of plants	1 kg from 12 plants
S5	U, T	BBCH 89	Grain	1 kg from 12 plants
			Straw	0.5 kg from 12 plants

DBA : Days before application  
DAA : Days after application

#### Location of the trial

The trial was performed on soil type and under cultural practices typical for oilseed rape production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Type of trial	Crop	European area	Region Country
1	C2103 AN1	Djamel BOUNAAS	DC	Winter wheat	North	Grand Est, France

DC: Decline curve

## Location



## Identity and composition of the test item(s):

### Test item

Trade or Code Name	CHR/H/CPD 300 SL
Active substance (a.s.)	Clopyralid
Formulation type	SL
CAS Number	[1702-17-6]
Nominal content of a.s.	300 g/L (expressed as clopyralid)
Batch number*	02/2018
Actual content *	30.18 %
Expiry date*	31/12/2022

## General Information on the trial

### Crop and soil Information

Trial No.	Crop	Variety	Crop density (kg/ha)	Sowing / Planting date	Soil type	pH	Organic matter (%)
C2103 AN1	Winter Wheat	Fructidor	180	14/10/2021	Silty clay	7.5	2.3

### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (cm)	Pressure (bars)
C2103 AN1	Agriser	Flat fan	Teejet XR 110015 VS	3	9	33	2.2

#### Summary of the actual application(s) data

Trial No.	Plot	Application No.	Active substance rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2103 AN1	T	1	130.0	+8.3	217	04/04/2022	29

#### Sampling of specimens

Trial No	Sampling	Actual Date	Actual DAA	Actual Growth Stage (BBCH)
C2103 AN1	1	04/04/2022	U : 0 DBA T : 0 DAA	29
	2	06/05/2022	32	39
	3	16/05/2022	42	59
	4	10/06/2022	67	77
	5	29/06/2022	86	89

DAA: Days after application

DBA: Days before application

#### ANALYTICAL PHASE

The objective of the analytical phase was to:

- determine residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in raw agricultural commodity (RAC) specimens generated during the field phase.
- demonstrate the applicability of the method to rest of plant and ears by concurrent recoveries (3 recoveries at LOQ and 3 recoveries at a higher level).

#### Experimental details

##### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trials.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table:

#### TRIAL No. C2103 AN1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2103 01 01	C2103 AN1 / U0 / A	04/04/2022	23/03/2023	353	25/03/2023	2
C2103 01 02	C2103 AN1 / T0 / A	04/04/2022	23/03/2023	353	07/04/2023	15
C2103 01 03	C2103 AN1 / T39 / A	06/05/2022	23/03/2023	321	07/04/2023	15
C2103 01 04	C2103 AN1 / T59 / A	16/05/2022	23/03/2023	311	07/04/2023	15
C2103 01 05	C2103 AN1 / T77E / A	10/06/2022	21/04/2023	315	25/04/2023	4
C2103 01 06	C2103 AN1 / T77R / A	10/06/2022	24/03/2023	287	14/04/2023	21
C2103 01 07	C2103 AN1 / UHG / A	29/06/2022	23/03/2023	267	25/03/2023	2
C2103 01 08	C2103 AN1 / UHS / A	29/06/2022	23/03/2023	267	25/03/2023	2
C2103 01 09	C2103 AN1 / THG / A	29/06/2022	21/04/2023	296	05/05/2023	14
C2103 01 10	C2103 AN1 / THS / A	29/06/2022	23/03/2023	267	14/04/2023	22

\*Frozen storage time of samples from sampling to extraction (days)

\*\* Refrigerated storage time of final extracts, from extraction to analysis (days)

#### Storage stability of extracts

After extraction, samples were stored refrigerated and analysed after maximum 15 days for whole plants, 4 days for ears, 21 days for rest of plants, 14 days for grain and 22 days for straw.

Results of storage stability of extracts in ANADIAG validation study No. C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities” showed a good stability of clopyralid residues for up to 15 days of refrigerated storage for high water content (whole plant) and dry commodities (grain and ears).

Reanalysis of a spiked sample showed good stability of extracts upon refrigerated storage after 15 days for whole plants, 21 days for rest of plants and 22 days for straw (see detailed stability data in Appendix V) as the recovery is within the acceptable interval (70-120%) (SANTE/2020/12830).

#### Storage stability of specimens

Specimens were stored frozen for no more than 353 days for whole plant and rest of plants, 315 days for ears and grain and 267 for straw from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in dry/high starch content commodities (straw) and for at least 13 months in whole plant, rest of plant, grain and ears (EFSA Journal Volume19, Issue1, January 2021, 6389).

#### Specimen analysis

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

Principle of the method

Residues of clopyralid and its conjugates were extracted and hydrolysed from samples by heating at 60 °C for 3 hours with 2.5M KOH. After acidification with H<sub>2</sub>SO<sub>4</sub>, addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract was purified with a liquid-liquid partition. An aliquot of the upper layer was evaporated to dryness and the sample was reconstituted in 50:50, methanol/H<sub>2</sub>O + 0.1% formic acid. Extracts were analysed by LC-MS/MS.

ANADIAG References (French version) of the method were

for the preparation and extraction of the samples: **SOP MP 718**

for the analysis of extracts and for the calibration: **SOP MA 1809**

#### LOD

**The limit of detection (LOD) was expressed as lowest calibration standard.**



**The LOD was 0.4 ng/mL for each matrix, corresponding to 0.002 mg/kg for clopyralid and 0.003 mg/kg for clopyralid glycine.**

#### **LOQ**

**The limit of quantification has been validated by fortifications at this level.**

**The LOQ was 0.01 mg/kg for each matrix and each analyte.**

#### **Preparation of standard solutions**

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

	<b>Solvent</b>	<b>Concentration</b>	<b>Storage conditions</b>	<b>Expiry date (Preparation + ...)</b>
<b>Stock solution Clopyralid</b>	Acetonitrile	≈ 1 mg/mL	Frozen	6 months
<b>Stock solution Clopyralid glycine</b>	Methanol	≈ 1 mg/mL	Frozen	6 months
<b>Spiking solutions Clopyralid glycine</b>	Acetonitrile	≈ 0.2 and 20 µg/mL	Frozen	1 month
<b>Intermediate calibration solutions Clopyralid</b>	Control extract	≈ 200 and 20 ng/mL	Refrigerated	14 days
<b>Matrix-matched Calibration solutions Clopyralid</b>	Control extract	≈ 0.4 to 24 ng/mL	Refrigerated	14 days

#### **Calibration curves**

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas obtained from chromatograms were plotted versus concentrations and the calibration functions were determined by least square fit.

Number and concentrations of standards used (min. 5 calibration levels), as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve (r) must be ≥ 0.990 for the calibration to be acceptable.

All extracts analysed (after dilution when required) fell within the range of the standard curve..

#### **Fortification procedure**

Fortifications were performed by adding known amounts of the spiking solutions to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

**Blank Samples:**

Analytical sample No.	Matrix	Clopyralid residues found (mg/kg)	Clopyralid glycine residues found (mg/kg)
C2103 01 01 11	Whole plants	NDR	NDR
C2103 01 07 11	Grain	NDR	NDR
C2103 01 08 11	Straw	NDR	NDR

**Spiked samples:**

Analytical Sample No.	Matrix	Fortification level (mg/kg)	% Recovery*	Extraction date	Storage time of extracts**	Spiked with
C2103 01 01 AA	Whole plants	0.01	86.1%	23/03/2023	2	Clopyralid
C2103 01 01 BA		0.01	72.5%	23/03/2023	2	Clopyralid glycine
C2103 01 01 CA		0.10	82.9%	23/03/2023	2	Clopyralid
C2103 01 01 DA		0.10	74.5%	23/03/2023	2	Clopyralid glycine
C2103 01 01 FA D100		10	77.6%	06/04/2023	1	Clopyralid glycine
C2103 01 07 AA	Grain	0.01	88.5%	23/03/2023	2	Clopyralid
C2103 01 07 BA		0.01	74.9%	23/03/2023	2	Clopyralid glycine
C2103 01 07 CA		0.10	89.7%	23/03/2023	2	Clopyralid
C2103 01 07 DA		0.10	72.1%	23/03/2023	2	Clopyralid glycine
C2103 01 07 GA D10		1.0	82.4%	21/04/2023	14	Clopyralid glycine
C2103 01 08 AA	Straw	0.01	82.9%	23/03/2023	2	Clopyralid
C2103 01 08 BA		0.01	65.9%	23/03/2023	2	Clopyralid glycine
C2103 01 08 CA		0.10	87.4%	23/03/2023	2	Clopyralid
C2103 01 08 DA		0.10	70.9%	23/03/2023	2	Clopyralid glycine
C2103 01 08 EA D10		1.0	74.0%	13/04/2023	1	Clopyralid glycine

\*Amount in control subtracted if above LOD.

\*\*Refrigerated storage time of final extracts, from extraction to analysis (days)

**Summary of recoveries – Concurrent recoveries**

Matrix	Fortification level (mg/kg)	Mean % recovery	Relative standard deviation %	Min % recovery	Max % recovery	Number of spiked samples	Spiked with
Rest of plants	0.01	92.1%	8.1%	87.6%	100.8%	3	Clopyralid
	0.01	80.2%	1.1%	79.7%	81.2%	3	Clopyralid glycine
	0.10	91.6%	0.8%	90.9%	92.4%	3	Clopyralid
	0.10	72.5%	3.6%	70.5%	75.4%	3	Clopyralid glycine
Ears	0.01	95.6%	3.6%	93.0%	99.5%	3	Clopyralid
	0.01	74.7%	4.9%	70.5%	77.4%	3	Clopyralid glycine
	0.10	93.6%	2.2%	91.2%	94.9%	3	Clopyralid
	0.10	84.6%	2.2%	82.5%	85.7%	3	Clopyralid glycine

For rest of plants and ears, recovery and repeatability (as precision, % RSD) data complied with the requirements of the SANTE/2020/12830, Rev.1 guideline as mean recoveries were within the range 60-120% with RSD less than 30% for spiked samples at 0.01 mg/kg and within the range 70-120% with RSD less than 20% for spiked samples at 0.10 mg/kg.

**Results**

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2103 AN1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2103 01 01	C2103 AN1 / U0 / A	-	Whole plants	-	NDR
C2103 01 02	C2103 AN1 / T0 / A	CHR/H/CPD 300 SL	Whole plants	0	7.01
C2103 01 03	C2103 AN1 / T39 / A	CHR/H/CPD 300 SL	Whole plants	32	0.70
C2103 01 04	C2103 AN1 / T59 / A	CHR/H/CPD 300 SL	Whole plants	42	0.59
C2103 01 05	C2103 AN1 / T77E / A	CHR/H/CPD 300 SL	Ears	67	0.75
C2103 01 06	C2103 AN1 / T77R / A	CHR/H/CPD 300 SL	Rest of plants	67	0.27
C2103 01 07	C2103 AN1 / UHG / A	-	Grain	-	NDR
C2103 01 08	C2103 AN1 / UHS / A	-	Straw	-	NDR
C2103 01 09	C2103 AN1 / THG / A	CHR/H/CPD 300 SL	Grain	86	0.34
C2103 01 10	C2103 AN1 / THS / A	CHR/H/CPD 300 SL	Straw	86	0.27

DAA: Days after last application

NDR: No detectable residues (residues below the limit of detection)

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

#### A 2.1.3.1.1.23 Study 23

Reference:	KCA 6.3/23
Report	Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Winter Wheat Following One Foliar application with FAWORYT 300 SL under Field Conditions in Northern Europe in 2022, E. Schneider, 2023, C2111, Anadiag, France
Guideline(s):	Regulation (EC) No. 1107/2009 Regulation (EU) No. 283/2013 and 284/2013 2004/10/EC GLP Directive OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021 SANTE/2019/12752 - Technical guidelines on data requirements for setting Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin. SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.
Deviations:	No
GLP:	Yes
Acceptability:	Yes

#### Objective of the study

The objective of the study was to determine the residue levels of Clopyralid (Sum of Clopyralid, its salts and conjugates) in Winter wheat raw agricultural commodity (RAC) after one foliar application of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at 1 site in Northern Europe. The trial was sampled frequently to monitor the decline of residues shortly after the treatment.

One plot was treated once with FAWORYT 300 SL at BBCH 29, at the application rate of 0.4 L/ha (120 g clopyralid/ha).

One plot remained untreated.

Sampling was performed at 0 DBA (Day Before application) on untreated plot and at 0 DAA (Days After Application) on the treated plot, then treated plot was sampled at BBCH 39, BBCH 59 and at BBCH 77. At BBCH 89 (at maturity of the crop) untreated and treated plots were sampled.

Clopyralid (Sum of Clopyralid, its salts and conjugates) residues were analysed in samples harvested during the field phase.

### Field phase description

The objective of the study was to determine the residue levels of Clopyralid (Sum of Clopyralid, its salts and conjugates) in Winter wheat raw agricultural commodity (RAC) after one foliar application of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

#### 1.1.1.1 Application details

Plot	Test Item(s)	Application No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	FAWORYT 300 SL	T1	BBCH 29	0.4 L/ha	120 g/ha	200-300 L/ha (±10%)

#### 1.1.1.2 Sampling Details

Sampling event	Plot	Timing	Matrix	Min. Sample size
S1	U	0 DBA	Whole plants	0.1 kg, 12 plants
	T	0 DAA	Whole plants	0.1 kg, 12 plants
S2	T	BBCH 39	Whole plants	0.2 kg, 12 plants
S3	T	BBCH 59	Whole plants	0.5 kg, 12 plants
S4	T	BBCH 77	Ears	0.5 kg from 12 plants
			Rest of plants	1 kg from 12 plants
S5	U, T	BBCH 89	Grain	1 kg from 12 plants
			Straw	0.5 kg from 12 plants

DBA : Days before application

DAA : Days after application

### Location of the trial

The trial was performed on soil type and under cultural practices typical for oilseed rape production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Type of trial	Crop	European area	Region, Country
1	C2111 CZ1	Iva SIMEK	DC	Winter wheat	North	Pardubicky, Czech Republic

DC: Decline curve

## Location



## Identity and composition of the test item(s):

### Test item

<b>Trade or Code Name</b>	<b>FAWORYT 300 SL</b>
<b>Active substance (a.s.)</b>	Clopyralid
<b>Formulation type</b>	SL
<b>CAS Number</b>	[1702-17-6]
<b>Nominal content of a.s.</b>	300 g/L (expressed as clopyralid)
<b>Batch number*</b>	202203001
<b>Actual content *</b>	302.2 g/L (expressed as clopyralid)
<b>Expiry date*</b>	11/03/2025

## General Information on the trial

### Crop and soil Information

Trial No.	Crop	Variety	Crop density (kg/ha)	Sowing / Planting date	Soil type	pH	Organic matter (%)
C2111 CZ1	Winter Wheat	BONANZA	170	11/10/2021	Clay	6.0	2.1

## Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (cm)	Pressure (bars)
C2111 CZ1	Pulvexper	Flat Fan	TEEJET XR 110 015 VS	3	9	33	2

### Summary of the actual application(s) data

Trial No.	Plot	Application No.	Active substance rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2111 CZ1	T	1	123.2	+ 2.7	257	20/04/2022	29

### Sampling of specimens

Trial No	Sampling	Actual Date	Actual DAA	Actual Growth Stage (BBCH)
C2111 CZ1	1	20/04/2022	U : 0 DBA T : 0 DAA	29
	2	20/05/2022	30	39
	3	05/06/2022	46	59
	4	23/06/2022	64	77
	5	02/08/2022	104	89

DAA: Days after application

DBA: Days before application

### ANALYTICAL PHASE

The objective of the analytical phase was to determine residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in raw agricultural commodity (RAC) specimens generated during the field phase.

### Experimental details

#### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trials.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table:

#### TRIAL No. C2111 CZ1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2111 01 01	C2111 CZ1 / U0 / A	20/04/2022	06/04/2023	351	07/04/2023	1
C2111 01 02	C2111 CZ1 / T0 / A	20/04/2022	06/04/2023	351	07/04/2023	1
C2111 01 03	C2111 CZ1 / T39 / A	20/05/2022	06/04/2023	321	19/04/2023	13
C2111 01 04	C2111 CZ1 / T59 / A	05/06/2022	06/04/2023	305	07/04/2023	1
C2111 01 05	C2111 CZ1 / T77E / A	23/06/2022	26/04/2023	307	05/05/2023	9
C2111 01 06	C2111 CZ1 / T77R / A	23/06/2022	19/04/2023	300	20/04/2023	1
C2111 01 07	C2111 CZ1 / UHG / A	02/08/2022	27/04/2023	268	05/05/2023	8
C2111 01 08	C2111 CZ1 / UHS / A	02/08/2022	02/05/2023	273	05/05/2023	3
C2111 01 09	C2111 CZ1 / THG / A	02/08/2022	27/04/2023	268	05/05/2023	8
C2111 01 10	C2111 CZ1 / THS / A	02/08/2022	02/05/2023	273	05/05/2023	3

\*Frozen storage time of samples from sampling to extraction (days)

\*\* Refrigerated storage time of final extracts, from extraction to analysis (days)



### **Storage stability of extracts**

After extraction, samples were stored below refrigerated and analysed after maximum 13 days for whole plants, 9 days for ears, 1 day for rest of plants, 8 days for grain and 3 days for straw.

Results of storage stability of extracts in ANADIAG validation study No. C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities” showed a good stability of clopyralid residues for up to 15 days of refrigerated storage for high water content (whole plant and rest of plants) and dry commodities (grain, straw and ears).

### **Storage stability of specimens**

Specimens were stored frozen for no more than 351 days for whole plant, 300 days for rest of plants, 307 days for ears and 268 days for grain and 273 for straw from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in dry/high starch content commodities (straw) and for at least 13 months in whole plant, rest of plant, grain and ears (EFSA Journal Volume19, Issue1, January 2021, e06389).

### **Specimen analysis**

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

The applicability of the method in rest of plants and ears was demonstrated in the ANADIAG study C2103 entitled “Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Winter Wheat Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022”

Principle of the method

Residues of clopyralid and its conjugates were extracted and hydrolysed from samples by heating at 60 °C for 3 hours with 2.5M KOH. After acidification with H<sub>2</sub>SO<sub>4</sub>, addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract was purified with a liquid-liquid partition. An aliquot of the upper layer was evaporated to dryness and the sample was reconstituted in 50:50, methanol/H<sub>2</sub>O + 0.1% formic acid. Extracts were analysed by LC-MS/MS.

ANADIAG References (French version) of the method were

for the preparation and extraction of the samples: **SOP MP 718**

for the analysis of extracts and for the calibration: **SOP MA 1809**

### **LOD**

**The limit of detection (LOD) was expressed as lowest calibration standard.**

**The LOD was 0.4 ng/mL for each matrix, corresponding to 0.002 mg/kg for clopyralid and 0.003 mg/kg for clopyralid glycine.**

### **LOQ**

**The limit of quantification has been validated by fortifications at this level.**

**The LOQ was 0.01 mg/kg for each matrix and each analyte.**

### **Preparation of standard solutions**

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.



	Solvent	Concentration	Storage conditions	Expiry date (Preparation + ...)
<b>Stock solution Clopyralid</b>	Acetonitrile	≈ 1 mg/mL	Frozen	6 months
<b>Stock solution Clopyralid glycine</b>	Methanol	≈ 1 mg/mL	Frozen	6 months
<b>Spiking solutions Clopyralid glycine</b>	Acetonitrile	≈ 0.2, 2, 20 or 200 µg/mL	Frozen	1 month
<b>Intermediate calibration solutions Clopyralid</b>	Control extract	≈ 200 and 20 ng/mL	Refrigerated	14 days
<b>Matrix-matched Calibration solutions Clopyralid</b>	Control extract	≈ 0.4 to 24 ng/mL	Refrigerated	14 days

### Calibration curves

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas obtained from chromatograms were plotted versus concentrations and the calibration functions were determined by least square fit.

Number and concentrations of standards used (min. 5 calibration levels), as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve (r) must be  $\geq 0.990$  for the calibration to be acceptable.

All extracts analysed (after dilution when required) fell within the range of the standard curve.

### Fortification procedure

Fortifications were performed by adding known amounts of the spiking solutions of clopyralid glycine to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts..

#### Blank Samples:

Analytical sample No.	Matrix	Clopyralid residues found (mg/kg)	Clopyralid glycine residues found (mg/kg)
S616 01 11	Whole plants	NDR	NDR
S607 01 11	Ears	NDR	NDR
S606 01 31	Rest of plants	NDR	NDR
S617 01 11	Grain	NDR	NDR
S618 01 11	Straw	NDR	NDR

#### Spiked samples:

Analytical Sample No.	Matrix	Fortification level (mg/kg)	% Recovery*	Extraction date	Storage time of extracts**	Spiked with
S616 01 AA	Whole plants	0.01	93.5%	05/04/2023	2	Clopyralid glycine
S616 01 BA D100		10	85.0%	06/04/2023	1	
S616 01 CB D200		20	73.0%	13/04/2023	6	
S607 01 AA	Ears	0.01	73.6%	26/04/2023	6	
S607 01 BA D10		1.0	93.2%	26/04/2023	7	
S607 01 CA d100		10	90.4%	09/05/2023	1	
S606 01 EA	Rest of plants	0.01	78.7%	28/04/2023	1	
S606 01 DA D10		0.99	71.5%	19/04/2023	1	
S617 01 CA	Grain	0.01	89.3%	16/05/2023	0	
S617 01 BA D10		1.0	75.1%	27/04/2023	8	
S618 01 AA	Straw	0.01	76.6%	28/04/2023	2	
S618 01 BA D10		1.0	84.0%	02/05/2023	3	

\*Amount in control subtracted if above LOD.

\*\*Refrigerated storage time of final extracts, from extraction to analysis (days)

#### Summary of recoveries – Concurrent recoveries

Matrix	Fortification level (mg/kg)	Mean % recovery	Relative standard deviation %	Min % recovery	Max % recovery	Number of spiked samples	Spiked with
Rest of plants	0.01	92.1%	8.1%	87.6%	100.8%	3	Clopyralid
	0.01	80.2%	1.1%	79.7%	81.2%	3	Clopyralid glycine
	0.10	91.6%	0.8%	90.9%	92.4%	3	Clopyralid
	0.10	72.5%	3.6%	70.5%	75.4%	3	Clopyralid glycine
Ears	0.01	95.6%	3.6%	93.0%	99.5%	3	Clopyralid
	0.01	74.7%	4.9%	70.5%	77.4%	3	Clopyralid glycine
	0.10	93.6%	2.2%	91.2%	94.9%	3	Clopyralid
	0.10	84.6%	2.2%	82.5%	85.7%	3	Clopyralid glycine

For rest of plants and ears, recovery and repeatability (as precision, % RSD) data complied with the requirements of the SANTE/2020/12830, Rev.1 guideline as mean recoveries were within the range 60-120% with RSD less than 30% for spiked samples at 0.01 mg/kg and within the range 70-120% with RSD less than 20% for spiked samples at 0.10 mg/kg.

#### Results

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2111 CZ1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2111 01 01	C2111 CZ1 / U0 / A	-	Whole plants	-	<b>NDR</b>
C2111 01 02	C2111 CZ1 / T0 / A	<b>FAWORYT 300 SL</b>	Whole plants	0	<b>6.74</b>
C2111 01 03	C2111 CZ1 / T39 / A	<b>FAWORYT 300 SL</b>	Whole plants	30	<b>2.43</b>
C2111 01 04	C2111 CZ1 / T59 / A	<b>FAWORYT 300 SL</b>	Whole plants	46	<b>1.37</b>
C2111 01 05	C2111 CZ1 / T77E / A	<b>FAWORYT 300 SL</b>	Ears	64	<b>1.17</b>
C2111 01 06	C2111 CZ1 / T77R / A	<b>FAWORYT 300 SL</b>	Rest of plants	64	<b>0.61</b>
C2111 01 07	C2111 CZ1 / UHG / A	-	Grain	-	<b>NDR</b>
C2111 01 08	C2111 CZ1 / UHS / A	-	Straw	-	<b>NDR</b>
C2111 01 09	C2111 CZ1 / THG / A	<b>FAWORYT 300 SL</b>	Grain	104	<b>0.36</b>
C2111 01 10	C2111 CZ1 / THS / A	<b>FAWORYT 300 SL</b>	Straw	104	<b>0.70</b>

DAA: Days after application

NDR: No detectable residues (residues below the limit of detection)

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

#### A 2.1.3.1.1.24 Study 24

Reference:	KCA 6.3/24
Report	Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Winter Wheat Following One Foliar application with FAWORYT 300 SL under Field Conditions in Northern Europe in 2022, E. Schneider, 2023, C2112, Anadiag, France
Guideline(s):	Regulation (EC) No. 1107/2009 Regulation (EU) No. 283/2013 and 284/2013 2004/10/EC GLP Directive OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021 SANTE/2019/12752 - Technical guidelines on data requirements for setting Maximum Residue Levels, comparability of residue trials and extrapolation of residue data on products from plant and animal origin. SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.
Deviations:	No
GLP:	Yes
Acceptability:	Yes

#### Objective of the study

The objective of the study was to determine the residue levels of Clopyralid (Sum of Clopyralid, its salts and conjugates) in Winter wheat raw agricultural commodity (RAC) after one foliar application of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at 1 site in Northern Europe. The trial was sampled at

harvest.

One plot was treated once with FAWORYT 300 SL at BBCH 29, at the application rate of 0.4 L/ha (120 g clopyralid/ha).

One plot remained untreated.

Sampling was performed at BBCH 89 (at maturity of the crop) in untreated and treated plots.

Clopyralid (Sum of Clopyralid, its salts and conjugates) residues were analysed in samples harvested during the field phase.

### Field phase description

The objective of the study was to determine the residue levels of Clopyralid (Sum of Clopyralid, its salts and conjugates) in Winter wheat raw agricultural commodity (RAC) after one foliar application of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

#### 1.1.1.1 Application details

Plot	Test Item(s)	Application No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	FAWORYT 300 SL	T1	BBCH 29	0.4 L/ha	120 g/ha	200-300 L/ha (±10%)

#### 1.1.1.2 Sampling Details

Sampling event	Plot	Timing	Matrix	Min. Sample size
S1	U, T	BBCH 89	Grain	1 kg from 12 plants
			Straw	0.5 kg from 12 plants

### Location of the trial

The trial was performed on soil type and under cultural practices typical for oilseed rape production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Type of trial	Crop	European area	Region Country
1	C2112 PL1	Krzysztof NOWAK	RH	Winter wheat	North	Lodzkie, Poland

RH : Residue at harvest

## Location



## Identity and composition of the test item(s):

### Test item

Trade or Code Name	FAWORYT 300 SL
Active substance (a.s.)	Clopyralid
Formulation type	SL
CAS Number	[1702-17-6]
Nominal content of a.s.	300 g/L (expressed as clopyralid)
Batch number*	202203001
Actual content *	302.2 g/L (expressed as clopyralid)
Expiry date*	11/03/2025

## General Information on the trial

### Crop and soil Information

Trial No.	Crop	Variety	Crop density (kg/ha)	Sowing / Planting date	Soil type	pH	Organic matter (%)
C2112 PL1	Winter Wheat	Plejada	150	21/09/2021	Sandy Clay	6.5	2.0

### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (cm)	Pressure (bars)
C2112 PL1	Euro-pulve	Flat fan	TEEJET XR 110 02 VS	3	9	33.33	3.0

#### Summary of the actual application(s) data

Trial No.	Plot	Application No.	Active substance rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2112 PL1	T	1	128.7	+ 7.2	322	26/04/2022	29

#### Sampling of specimens

Trial No	Sampling	Actual Date	Actual DAA	Actual Growth Stage (BBCH)
C2112 PL1	1	28/07/2022	93	89

DAA: Days After Application

#### ANALYTICAL PHASE

The objective of the analytical phase was to determine residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in raw agricultural commodity (RAC) specimens generated during the field phase.

#### Experimental details

##### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trials.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table:

##### TRIAL No. C2112 PL1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2112 01 01	C2112 PL1 / UHG / A	28/07/2022	27/04/2023	273	05/05/2023	8
C2112 01 02	C2112 PL1 / UHS / A	28/07/2022	02/05/2023	278	05/05/2023	3
C2112 01 03	C2112 PL1 / THG / A	28/07/2022	27/04/2023	273	05/05/2023	8
C2112 01 04	C2112 PL1 / THS / A	28/07/2022	02/05/2023	278	05/05/2023	3

\*Frozen storage time of samples from sampling to extraction (days)

\*\* Refrigerated storage time of final extracts, from extraction to analysis (days)

#### Storage stability of extracts

After extraction, samples were stored below refrigerated and analysed after maximum 8 days for grain and 3 days for straw.

Results of storage stability of extracts in ANADIAG validation study No. C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities” showed a good stability of clopyralid residues for up to 15 days of refrigerated storage for dry commodities (grain and straw).

#### Storage stability of specimens

Specimens were stored frozen for no more than 273 days for grain and 278 days for straw from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in dry/high starch content commodities (straw) and for at least 13 months in grain (EFSA Journal Volume19, Issue1, January 2021, e06389).

### Specimen analysis

Samples were analysed according to the method developed by ANADIAG and validated under ANADI-AG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

#### Principle of the method

Residues of clopyralid and its conjugates were extracted and hydrolysed from samples by heating at 60 °C for 3 hours with 2.5M KOH. After acidification with H<sub>2</sub>SO<sub>4</sub>, addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract was purified with a liquid-liquid partition. An aliquot of the upper layer was evaporated to dryness and the sample was reconstituted in 50:50, methanol/H<sub>2</sub>O + 0.1% formic acid. Extracts were analysed by LC-MS/MS.

ANADIAG References (French version) of the method were

for the preparation and extraction of the samples: **SOP MP 718**

for the analysis of extracts and for the calibration: **SOP MA 1809**

### LOD

The limit of detection (LOD) was expressed as lowest calibration standard.

The LOD was 0.4 ng/mL for each matrix, corresponding to 0.002 mg/kg for clopyralid and 0.003 mg/kg for clopyralid glycine.

### LOQ

The limit of quantification has been validated by fortifications at this level.

The LOQ was 0.01 mg/kg for each matrix and each analyte.

### Preparation of standard solutions

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

	Solvent	Concentration	Storage conditions	Expiry date (Preparation + ...)
Stock solution Clopyralid	Acetonitrile	≈ 1 mg/mL	Frozen	6 months
Stock solution Clopyralid glycine	Methanol	≈ 1 mg/mL	Frozen	6 months
Spiking solutions Clopyralid glycine	Acetonitrile	≈ 0.2 and 20 µg/mL	Frozen	1 month
Intermediate calibration solutions Clopyralid	Control extract	≈ 200 and 20 ng/mL	Refrigerated	14 days
Matrix-matched Calibration solutions Clopyralid	Control extract	≈ 0.4 to 24 ng/mL	Refrigerated	14 days

### Calibration curves

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas obtained from chromatograms were plotted versus concentrations and the calibration functions were determined by least square fit.

Number and concentrations of standards used (min. 5 calibration levels), as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve (r) must be ≥ 0.990 for the calibration to be acceptable.

All extracts analysed (after dilution when required) fell within the range of the standard curve.

### Fortification procedure

Fortifications were performed by adding known amounts of the spiking solutions of clopyralid glycine to control specimens just prior to the extraction step (spiking solutions were added to the control specimens,



before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.

**Blank Samples:**

Analytical sample No.	Matrix	Clopyralid residues found (mg/kg)	Clopyralid glycine residues found (mg/kg)
S617 01 11	Grain	NDR	NDR
S618 01 11	Straw	NDR	NDR

**Spiked samples:**

Analytical Sample No.	Matrix	Fortification level (mg/kg)	% Recovery*	Extraction date	Storage time of extracts**	Spiked with
S617 01 CA	Grain	0.01	89.3%	16/05/2023	0	Clopyralid glycine
S617 01 BA D10		1.0	75.1%	27/04/2023	8	
S618 01 AA	Straw	0.01	76.6%	28/04/2023	2	
S618 01 BA D10		1.0	84.0%	02/05/2023	3	

\*Amount in control subtracted if above LOD.

\*\*Refrigerated storage time of final extracts, from extraction to analysis (days)

**Results**

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2112 PL1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2112 01 01	C2112 PL1 / UHG / A	-	Grain	-	NDR
C2112 01 02	C2112 PL1 / UHS / A	-	Straw	-	NDR
C2112 01 03	C2112 PL1 / THG / A	FAWORYT 300 SL	Grain	93	0.85
C2112 01 04	C2112 PL1 / THS / A	FAWORYT 300 SL	Straw	93	0.93

DAA: Days after application

NDR: No detectable residues (residues below the limit of detection)

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

**A 2.1.3.1.1.25 Study 25**

Reference: KCA 6.3/25

Report Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Winter Wheat Following One Foliar application with FAWORYT 300 SL under Field Conditions in Northern Europe in 2022, E. Schneider, 2023, C2118, Anadiag, France

Guideline(s): Regulation (EC) No. 1107/2009  
Regulation (EU) No. 283/2013 and 284/2013  
2004/10/EC GLP Directive  
OECD – guideline for the testing of chemicals, 509; Crop field trial, 14/06/2021  
SANTE/2019/12752 - Technical guidelines on data requirements for setting Maximum Residue Levels, comparability of residue trials and extrapolation

of residue data on products from plant and animal origin.  
SANTE/2020/12830 Rev.1, 24/02/2021 - Guidance Document on Pesticide Analytical Methods for Risk Assessment and Post-approval Control and Monitoring Purposes  
OECD series on testing and assessment No. 72 and series on pesticides No. 39; Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17, 13/08/2007.

**Deviations:**

**Deviation No. 03/06/2022**

Trial C2118 ND1:

At sampling No.3 (BBCH 59), the whole plants (no roots) were cut at 15 cm above soil level instead of at soil level as required by the study plan.

According to the study plan, it is only allowed to cut plants at 15 cm above the soil after BBCH 59.

The deviation was due to an error of the principal investigator.

The deviation has no impact on the study as it concerns a sampling at an immature growth stage of the crop. Moreover no impact on the study as the whole plants were high enough (70 cm). The residue level may have not been impacted significantly. The deviation remained within the range of  $\pm 25\%$  allowed by OECD guideline 509 for the testing of Chemicals

**GLP:**

Yes

**Acceptability:**

Yes

**Objective of the study**

The objective of the study was to determine the residue levels of Clopyralid (Sum of Clopyralid, its salts and conjugates) in Winter wheat raw agricultural commodity (RAC) after one foliar application of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

The study consisted of two phases: the field phase and the analytical phase.

The study was conducted under field conditions at 1 site in Northern Europe. The trial was sampled frequently to monitor the decline of residues shortly after the treatment.

One plot was treated once with FAWORYT 300 SL at BBCH 29, at the application rate of 0.4 L/ha (120 g clopyralid/ha).

One plot remained untreated.

Sampling was performed at 0 DBA (Day Before application) on untreated plot and at 0 DAA (Days After Application) on the treated plot, then treated plot was sampled at BBCH 39, BBCH 59 and at BBCH 77.

At BBCH 89 (at maturity of the crop) untreated and treated plots were sampled.

Clopyralid (Sum of Clopyralid, its salts and conjugates) residues were analysed in samples harvested during the field phase.

**Field phase description**

The objective of the study was to determine the residue levels of Clopyralid (Sum of Clopyralid, its salts and conjugates) in Winter wheat raw agricultural commodity (RAC) after one foliar application of the formulated product FAWORYT 300 SL (300 g clopyralid/L), at the rate of 0.4 L/ha.

#### 1.1.1.1 Application details

Plot	Test Item(s)	Application No.	Target Timing	Application Rate of the Formulated Product	Application Rate of the active substance	Spray volume
U	Untreated	--	--	--	--	--
T	<b>FAWORYT 300 SL</b>	T1	BBCH 29	0.4 L/ha	120 g/ha	200-300 L/ha (±10%)

#### 1.1.1.2 Sampling Details

Sampling event	Plot	Timing	Matrix	Min. Sample size
<b>S1</b>	U	0 DBA	Whole plants	0.1 kg, 12 plants
	T	0 DAA	Whole plants	0.1 kg, 12 plants
<b>S2</b>	T	BBCH 39	Whole plants	0.2 kg, 12 plants
<b>S3</b>	T	BBCH 59	Whole plants	0.5 kg, 12 plants
<b>S4</b>	T	BBCH 77	Ears	0.5 kg from 12 plants
			Rest of plants	1 kg from 12 plants
<b>S5</b>	U, T	BBCH 89	Grain	1 kg from 12 plants
			Straw	0.5 kg from 12 plants

DBA : Days before application

DAA : Days after application

#### Location of the trial

The trial was performed on soil type and under cultural practices typical for oilseed rape production and on a typical cultivar of the regional commercial production.

	Trial No.	Principal Investigator	Type of trial	Crop	European area	Region, Country
<b>1</b>	<b>C2118 ND1</b>	Rémi DUTERTE	DC	Winter wheat	North	Hauts-de-France, France

DC: Decline curve

## Location



## Identity and composition of the test item(s):

### Test item

Trade or Code Name	FAWORYT 300 SL
Active substance (a.s.)	Clopyralid
Formulation type	SL
CAS Number	[1702-17-6]
Nominal content of a.s.	300 g/L (expressed as clopyralid)
Batch number*	202203001
Actual content *	302.2 g/L (expressed as clopyralid)
Expiry date*	11/03/2025

## General Information on the trial

### Crop and soil Information

Trial No.	Crop	Variety	Crop density (kg/ha)	Sowing / Planting date	Soil type	pH	Organic matter (%)
C2118 ND1	Winter Wheat	PORTHUS	180	26/11/2021	Loam	7.5	2.2

### Application equipment

Trial No.	Sprayer type	Type of nozzles	Model of the nozzles	Length of the boom (m)	Number of nozzles	Distance Between nozzles (cm)	Pressure (bars)
C2118 ND1	Pulvexper	Flat Fan	TEEJET XR 110 015 VS	3	9	33	2

#### Summary of the actual application(s) data

Trial No.	Plot	Application No.	Active substance rate (g/ha)	Deviation from the intended application rate (%)	Spray volume (L/ha)	Date	Growth stage (BBCH)
C2118 ND1	T	1	124.0	+ 3.3	207	18/04/2022	29

#### Sampling of specimens

Trial No	Sampling	Actual Date	Actual DAA	Actual Growth Stage (BBCH)
C2118 ND1	1	18/04/2022	U : 0 DBA T : 0 DAA	29
	2	18/05/2022	30	39
	3	01/06/2022	44	59
	4	07/07/2022	80	77
	5	25/07/2022	98	89

DAA: Days after application

DBA: Days before application

#### ANALYTICAL PHASE

The objective of the analytical phase was to determine residue levels of clopyralid (Sum of clopyralid, its salts and conjugates (ie clopyralid glycine conjugates)) in raw agricultural commodity (RAC) specimens generated during the field phase.

#### Experimental details

##### Reference item(s)

Clopyralid, 99.50%, Sigma-Aldrich, Expiry date 31/01/2026

Clopyralid glycine, 98.53%, Synthex Technologies, Expiry date 01/10/2023

Field specimens were collected, frozen and dispatched to ANADIAG laboratory for residue analysis by the persons in charge of the field trials.

The specimens were treated according to ANADIAG SOPs for receipt, identification and storage.

Analytical references and storage time are summarized in the following table:

### TRIAL No. C2118 ND1

Analytical Sample No.	Field Sample No.	Harvest / Sampling Date	Extraction Date	Storage time of samples*	Analysis date	Storage time of extracts**
C2118 01 01	C2118 ND1 / U0 / A	18/04/2022	05/04/2023	352	07/04/2023	2
C2118 01 02	C2118 ND1 / T0 / A	18/04/2022	05/04/2023	352	07/04/2023	2
C2118 01 03	C2118 ND1 / T39 / A	18/05/2022	05/04/2023	322	07/04/2023	2
C2118 01 04	C2118 ND1 / T59 / A	01/06/2022	05/04/2023	308	07/04/2023	2
C2118 01 05	C2118 ND1 / T77E / A	07/07/2022	26/04/2023	293	03/05/2023	7
C2118 01 06	C2118 ND1 / T77R / A	07/07/2022	19/04/2023	286	20/04/2023	1
C2118 01 07	C2118 ND1 / UHG / A	25/07/2022	27/04/2023	276	05/05/2023	8
C2118 01 08	C2118 ND1 / UHS / A	25/07/2022	28/04/2023	277	30/04/2023	2
C2118 01 09	C2118 ND1 / THG / A	25/07/2022	27/04/2023	276	05/05/2023	8
C2118 01 10	C2118 ND1 / THS / A	25/07/2022	28/04/2023	277	30/04/2023	2

\*Frozen storage time of samples from sampling to extraction (days)

\*\* Refrigerated storage time of final extracts, from extraction to analysis (days)

### Storage stability of extracts

After extraction, samples were stored below refrigerated and analysed after maximum 2 days for whole plants, 7 days for ears, 1 day for rest of plants, 8 days for grain and 2 days for straw.

Results of storage stability of extracts in ANADIAG validation study No. C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities” showed a good stability of clopyralid residues for up to 15 days of refrigerated storage for high water content (whole plant and rest of plants) and dry commodities (grain, straw and ears).

### Storage stability of specimens

Specimens were stored frozen for no more than 352 days for whole plant, 286 days for rest of plants, 293 days for ears and 276 days for grain and 277 for straw from sampling to extraction.

Residues of active ingredient in this matrix/crop group have been shown to be stable under these conditions for at least 10 months in dry/high starch content commodities (straw) and for at least 13 months in whole plant, rest of plant, grain and ears (EFSA Journal Volume 19, Issue 1, January 2021, e06389).

### Specimen analysis

Samples were analysed according to the method developed by ANADIAG and validated under ANADIAG study No C2135 entitled “Validation of the Analytical Method for the Analysis of Clopyralid (Sum of Clopyralid, its salts and conjugates) in High water content, in High Oil content and Dry Commodities.

The applicability of the method in rest of plants and ears was demonstrated in the ANADIAG study C2103 entitled “Determination of Clopyralid (Sum of Clopyralid, its salts and conjugates) Residues in Winter Wheat Following One Foliar application with CHR/H/CPD 300 SL under Field Conditions in Northern Europe in 2022”

#### Principle of the method

Residues of clopyralid and its conjugates were extracted and hydrolysed from samples by heating at 60 °C for 3 hours with 2.5M KOH. After acidification with H<sub>2</sub>SO<sub>4</sub>, addition of acetonitrile, magnesium sulfate and sodium chloride, the raw extract was purified with a liquid-liquid partition. An aliquot of the upper layer was evaporated to dryness and the sample was reconstituted in 50:50, methanol/H<sub>2</sub>O + 0.1% formic acid. Extracts were analysed by LC-MS/MS.

ANADIAG References (French version) of the method were

for the preparation and extraction of the samples: **SOP MP 718**

for the analysis of extracts and for the calibration: **SOP MA 1809**

### LOD

**The limit of detection (LOD) was expressed as lowest calibration standard.**

**The LOD was 0.4 ng/mL for each matrix, corresponding to 0.002 mg/kg for clopyralid and 0.003 mg/kg for clopyralid glycine.**

#### **LOQ**

**The limit of quantification has been validated by fortifications at this level.**

**The LOQ was 0.01 mg/kg for each matrix and each analyte.**

#### **Preparation of standard solutions**

Calibration and spiking solutions were prepared by dilution of a stock solution resulting from a commercial reference item.

	<b>Solvent</b>	<b>Concentration</b>	<b>Storage conditions</b>	<b>Expiry date (Preparation + ...)</b>
<b>Stock solution Clopyralid</b>	Acetonitrile	≈ 1 mg/mL	Frozen	6 months
<b>Stock solution Clopyralid glycine</b>	Methanol	≈ 1 mg/mL	Frozen	6 months
<b>Spiking solutions Clopyralid glycine</b>	Acetonitrile	≈ 0.2, 2, 20 or 200 µg/mL	Frozen	1 month
<b>Intermediate calibration solutions Clopyralid</b>	Control extract	≈ 200 and 20 ng/mL	Refrigerated	14 days
<b>Matrix-matched Calibration solutions Clopyralid</b>	Control extract	≈ 0.4 to 24 ng/mL	Refrigerated	14 days

#### **Calibration curves**

Aliquots of the calibration solutions were injected into the analytical system using the same conditions as the specimens.

Peak areas obtained from chromatograms were plotted versus concentrations and the calibration functions were determined by least square fit.

Number and concentrations of standards used (min. 5 calibration levels), as well as acceptability criteria are described in SOP No. PG 0118. According to this SOP, the correlation coefficient for a curve (r) must be ≥ 0.990 for the calibration to be acceptable.

All extracts analysed (after dilution when required) fell within the range of the standard curve.

#### **Fortification procedure**

Fortifications were performed by adding known amounts of the spiking solutions of clopyralid glycine to control specimens just prior to the extraction step (spiking solutions were added to the control specimens, before mixing with the extraction solvent).

During the residue analysis, control samples were fortified, extracted and stored together with field samples until analysis. These fortified extracts were run during the analysis of the other extracts.



#### Blank Samples:

Analytical sample No.	Matrix	Clopyralid residues found (mg/kg)	Clopyralid glycine residues found (mg/kg)
S616 01 11	Whole plants	NDR	NDR
S607 01 11	Ears	NDR	NDR
S606 01 31	Rest of plants	NDR	NDR
S617 01 11	Grain	NDR	NDR
S618 01 11	Straw	NDR	NDR

#### Spiked samples:

Analytical Sample No.	Matrix	Fortification level (mg/kg)	% Recovery*	Extraction date	Storage time of extracts**	Spiked with
S616 01 AA	Whole plants	0.01	93.5%	05/04/2023	2	Clopyralid glycine
S616 01 BA D100		10	85.0%	06/04/2023	1	
S616 01 CB D200		20	73.0%	13/04/2023	6	
S607 01 AA	Ears	0.01	73.6%	26/04/2023	6	
S607 01 BA D10		1.0	93.2%	26/04/2023	7	
S607 01 CA d100		10	90.4%	09/05/2023	1	
S606 01 EA	Rest of plants	0.01	78.7%	28/04/2023	1	
S606 01 DA D10		0.99	71.5%	19/04/2023	1	
S617 01 CA	Grain	0.01	89.3%	16/05/2023	0	
S617 01 BA D10		1.0	75.1%	27/04/2023	8	
S618 01 AA	Straw	0.01	76.6%	28/04/2023	2	
S618 01 BA D10		1.0	84.0%	02/05/2023	3	

\*Amount in control subtracted if above LOD.

\*\*Refrigerated storage time of final extracts, from extraction to analysis (days)

## Results

The analytical results obtained are summarized in the table below.

**Table 1 TRIAL No. C2118 ND1**

Analytical sample No.	Field sample No.	Treatment	Matrix	DAA	Clopyralid residues found (mg/kg)
C2118 01 01	C2118 ND1 / U0 / A	-	Whole plants	-	NDR
C2118 01 02	C2118 ND1 / T0 / A	FAWORYT 300 SL	Whole plants	0	7.78
C2118 01 03	C2118 ND1 / T39 / A	FAWORYT 300 SL	Whole plants	30	0.58
C2118 01 04	C2118 ND1 / T59 / A	FAWORYT 300 SL	Whole plants	44	0.48
C2118 01 05	C2118 ND1 / T77E / A	FAWORYT 300 SL	Ears	80	0.34
C2118 01 06	C2118 ND1 / T77R / A	FAWORYT 300 SL	Rest of plants	80	0.25
C2118 01 07	C2118 ND1 / UHG / A	-	Grain	-	NDR
C2118 01 08	C2118 ND1 / UHS / A	-	Straw	-	NDR
C2118 01 09	C2118 ND1 / THG / A	FAWORYT 300 SL	Grain	98	0.26
C2118 01 10	C2118 ND1 / THS / A	FAWORYT 300 SL	Straw	98	0.50

DAA: Days after application

NDR: No detectable residues (residues below the limit of detection)

LOD = 0.002 mg/kg

LOQ = 0.01 mg/kg

#### **A 2.1.4            Magnitude of residues in processed commodities (Industrial Processing and/or Household Preparation)**

##### **A 2.1.4.1           Processing studies on a core set of representative processes**

Data matching studies have been evaluated by RMS - Finland. As a result of the assessment all reports were accepted and considered as equivalent to protected studies. Therefore, to support the renewal of authorization of CHR/H/CPD300SL/Major 300SL, Cloe 300SL, ProSto 300SL INNVIGO is allowed to refer to EU approved reports.


##### **A 2.1.5            Magnitude of residues in representative succeeding crops**

No new studies submitted.


##### **A 2.1.6            Other/special studies**

No new studies submitted.


## Appendix 3 Pesticide Residue Intake Model (PRIMo) TMDI calculations

 European Food Safety Authority EFSA PRIMo revision 3.1; 2019/03/19		<b>clopyralid (F)</b>		Input values							
		LOQs (mg/kg) range from: to:		Details - chronic risk assessment							
		<b>Toxicological reference values</b>		Supplementary results - chronic risk assessment							
		ADI (mg/kg bw/day):	0.15	ARID (mg/kg bw):	0.17						
Source of ADI:		Source of ARID:		Details - acute risk assessment/children							
Year of evaluation:		Year of evaluation:		Details - acute risk assessment/adults							
Comments:											
Normal mode											
Chronic risk assessment: JMPR methodology (IEDI/TMDI)											
		No of diets exceeding the ADI: ---									
TMDI/IEDI calculation (based on average food consumption)	Calculated exposure (% of ADI)	MS Diet (% of ADI)	Exposure (µg/kg bw per day)	Highest contributor to MS diet (in % of ADI)	Commodity / group of commodities	2nd contributor to MS diet (in % of ADI)	Commodity / group of commodities	3rd contributor to MS diet (in % of ADI)	Commodity / group of commodities	Exposure resulting from MRLs set at the LOQ (in % of ADI)	commodities not under assessment (in % of ADI)
	15%	GEMS/Food G06	23.20	14%	Wheat	1.0%	Sugar beet roots	0.0%	Rapeseeds/canola seeds		
	14%	NL child	21.00	8%	Wheat	6%	Sugar beet roots	0.2%	Rapeseeds/canola seeds		
	13%	IT toddler	19.94	13%	Wheat		Grapefruits				
	12%	NL toddler	17.55	8%	Wheat	3%	Sugar beet roots	0.3%	Rapeseeds/canola seeds		
	12%	FR child 3-15 yr	17.48	9%	Wheat	2%	Sugar beet roots	0.0%	Rapeseeds/canola seeds		
	11%	RO general	16.52	10%	Wheat	0.9%	Sugar beet roots				
	10%	UK toddler	14.96	8%	Wheat	2%	Sugar beet roots				
	9%	GEMS/Food G15	13.73	9%	Wheat	0.1%	Rapeseeds/canola seeds				
	9%	ES child	13.48	9%	Wheat	0.1%	Sugar beet roots				
	9%	DK child	13.25	9%	Wheat	0.0%	Rapeseeds/canola seeds				
	9%	GEMS/Food G07	12.93	8%	Wheat	0.2%	Rapeseeds/canola seeds	0.0%	Sugar beet roots		
	8%	DE child	12.61	8%	Wheat	0.0%	Rapeseeds/canola seeds				
	8%	GEMS/Food G08	12.41	8%	Wheat	0.1%	Rapeseeds/canola seeds				
	8%	IT adult	12.41	8%	Wheat		Grapefruits				
	8%	FR toddler 2-3 yr	12.07	6%	Wheat	2%	Sugar beet roots	0.0%	Rapeseeds/canola seeds		
	8%	GEMS/Food G10	11.89	8%	Wheat	0.1%	Rapeseeds/canola seeds	0.0%	Sugar beet roots		
	8%	PT general	11.76	8%	Wheat		Grapefruits				
	7%	DE women 14-50 yr	11.03	4%	Wheat	3%	Sugar beet roots	0.0%	Rapeseeds/canola seeds		
	7%	GEMS/Food G11	10.82	7%	Wheat		Grapefruits				
	7%	DE general	9.88	4%	Wheat	3%	Sugar beet roots	0.0%	Rapeseeds/canola seeds		
	6%	SE general	9.61	6%	Wheat		Grapefruits				
	6%	UK infant	9.27	5%	Wheat	0.9%	Sugar beet roots				
	6%	NL general	8.80	4%	Wheat	2%	Sugar beet roots	0.1%	Rapeseeds/canola seeds		
	5%	FR adult	7.48	4%	Wheat	0.5%	Sugar beet roots	0.0%	Rapeseeds/canola seeds		
	5%	ES adult	7.18	5%	Wheat	0.1%	Sugar beet roots				
	5%	IE adult	6.89	5%	Wheat		Grapefruits				
	4%	UK vegetarian	6.67	4%	Wheat	0.4%	Sugar beet roots				
	4%	UK adult	5.59	3%	Wheat	0.4%	Sugar beet roots				
	2%	FR infant	3.71	2%	Wheat	0.9%	Sugar beet roots	0.0%	Rapeseeds/canola seeds		
	2%	FI 3 yr	3.62	2%	Wheat	0.0%	Rapeseeds/canola seeds				
	2%	IE child	3.49	2%	Wheat		Grapefruits				
	2%	DK adult	3.37	2%	Wheat		Grapefruits				
	2%	LT adult	3.16	2%	Wheat		Grapefruits				
	2%	FI 6 yr	2.95	2%	Wheat	0.0%	Rapeseeds/canola seeds				
	0.6%	FI adult	0.96	0.6%	Wheat	0.0%	Rapeseeds/canola seeds				
Column7				Grapefruits							
<b>Conclusion:</b> The estimated long-term dietary intake (TMDI/IEDI) was below the ADI. The long-term intake of residues of clopyralid (F) is unlikely to present a public health concern.											

## IEDI calculations- updated

 European Food Safety Authority EFSA PRIMo revision 3.1; 2019/03/19		<b>clopyralid (F)</b>		Input values							
		LOQs (mg/kg) range from: to:		Details - chronic risk assessment							
		<b>Toxicological reference values</b>		Supplementary results - chronic risk assessment							
		ADI (mg/kg bw/day):	0.15	ARID (mg/kg bw):	0.17						
Source of ADI:		Source of ARID:		Details - acute risk assessment/children							
Year of evaluation:		Year of evaluation:		Details - acute risk assessment/adults							
Comments:											
Normal mode											
Chronic risk assessment: JMPR methodology (IEDI/TMDI)											
No of diets exceeding the ADI: ---											
TMDI/IEDI calculation (based on average food consumption)	Calculated exposure (% of ADI)	MS Diet (% of ADI)	Exposure (µg/kg bw per day)	Highest contributor to MS diet (in % of ADI)	Commodity / group of commodities	2nd contributor to MS diet (in % of ADI)	Commodity / group of commodities	3rd contributor to MS diet (in % of ADI)	Commodity / group of commodities	Exposure resulting from MRLs set at the LOQ (in % of ADI)	commodities not under assessment (in % of ADI)
	4%	NL child	5.59	2%	Wheat	2%	Sugar beet roots	0.0%	Rapeseeds/canola seeds		
	4%	GEMS/Food G06	5.54	3%	Wheat	0.3%	Sugar beet roots	0.0%	Rapeseeds/canola seeds		
	3%	IT toddler	4.65	3%	Wheat		Grapefruits				
	3%	NL toddler	4.46	2%	Wheat	1%	Sugar beet roots	0.0%	Rapeseeds/canola seeds		
	3%	FR child 3-15 yr	4.39	2%	Wheat	0.8%	Sugar beet roots	0.0%	Rapeseeds/canola seeds		
	3%	RO general	3.97	2%	Wheat	0.3%	Sugar beet roots				
	3%	UK toddler	3.77	2%	Wheat	0.7%	Sugar beet roots				
	2%	GEMS/Food G15	3.19	2%	Wheat	0.0%	Rapeseeds/canola seeds				
	2%	ES child	3.16	2%	Wheat	0.0%	Sugar beet roots				
	2%	DK child	3.09	2%	Wheat	0.0%	Rapeseeds/canola seeds				
	2%	FR toddler 2-3 yr	3.06	1%	Wheat	0.6%	Sugar beet roots	0.0%	Rapeseeds/canola seeds		
	2%	DE women 14-50 yr	2.97	1%	Wheat	1.0%	Sugar beet roots	0.0%	Rapeseeds/canola seeds		
	2%	GEMS/Food G07	2.97	2%	Wheat	0.0%	Rapeseeds/canola seeds	0.0%	Sugar beet roots		
	2%	DE child	2.94	2%	Wheat	0.0%	Rapeseeds/canola seeds				
	2%	IT adult	2.89	2%	Wheat		Grapefruits				
	2%	GEMS/Food G08	2.87	2%	Wheat	0.0%	Rapeseeds/canola seeds				
	2%	GEMS/Food G10	2.75	2%	Wheat	0.0%	Rapeseeds/canola seeds	0.0%	Sugar beet roots		
	2%	PT general	2.74	2%	Wheat		Grapefruits				
	2%	DE general	2.67	0.9%	Sugar beet roots	0.9%	Wheat				
	2%	GEMS/Food G11	2.52	2%	Wheat	0.3%	Sugar beet roots				
	2%	UK infant	2.29	1%	Wheat	0.6%	Sugar beet roots	0.0%	Rapeseeds/canola seeds		
	2%	NL general	2.28	0.9%	Wheat		Grapefruits				
	1%	SE general	2.24	1%	Wheat	0.2%	Sugar beet roots	0.0%	Rapeseeds/canola seeds		
	1%	FR adult	1.81	1%	Wheat	0.0%	Sugar beet roots				
	1%	ES adult	1.69	1%	Wheat		Grapefruits				
	1%	IE adult	1.61	1%	Wheat	0.1%	Sugar beet roots				
	1%	UK vegetarian	1.60	1.0%	Wheat	0.1%	Sugar beet roots	0.0%	Rapeseeds/canola seeds		
	0.9%	UK adult	1.35	0.8%	Wheat	0.3%	Sugar beet roots				
	0.7%	FR infant	0.98	0.4%	Wheat	0.0%	Rapeseeds/canola seeds				
	0.6%	FI 3 yr	0.84	0.6%	Wheat	0.81	0.5%	Wheat			
	0.5%	IE child	0.81	0.5%	Wheat		Grapefruits				
	0.5%	DK adult	0.79	0.5%	Wheat		Grapefruits				
	0.5%	LT adult	0.74	0.5%	Wheat	0.0%	Rapeseeds/canola seeds				
	0.5%	FI 6 yr	0.68	0.5%	Wheat	0.0%	Rapeseeds/canola seeds				
	0.1%	FI adult	0.22	0.1%	Wheat		Grapefruits				
Column7				Grapefruits							
Conclusion:						The estimated long-term dietary intake (TMDI/IEDI) was below the ADI. The long-term intake of residues of clopyralid (F) is unlikely to present a public health concern.					

New calculations:

<div></div> <div>European Food Safety Authority</div> <div>EFSA PRIMA revision 5.1, 2019/03/19</div>		<div>clopyralid (F)</div> <div>EC(Reg) (single beam): 10</div> <div>Toxicological reference values</div> <div>ADI (mg/kg bw/day): 0.15</div> <div>Source of ADI: EFSA PRIMA</div> <div>Year of evaluation: 2019</div> <div>EC(Reg) (single beam): 0.17</div> <div>Source of MRL: EFSA PRIMA</div> <div>Year of evaluation: 2019</div>				<div>Input values</div> <div>Details - chronic risk assessment</div> <div>Supplementary results - chronic risk assessment</div> <div>Details - acute risk assessment/children</div> <div>Details - acute risk assessment/adults</div>					
		Comments:									
		Normal mode									
		Chronic risk assessment: JMPR methodology (IED/TMDI)									
No. of diets exceeding the ADI: ---											
TMDI (IED) calculation (based on average food consumption)	Calculated exposure (% of ADI)	MS Diet	Exposure (µg/kg bw per day)	Highest contributor to MS diet (% of ADI)	Commodity / group of commodities	2nd contributor to MS diet (% of ADI)	Commodity / group of commodities	3rd contributor to MS diet (% of ADI)	Commodity / group of commodities	MRLs set at the LOQ (in % of ADI)	Commodities not under assessment (in % of ADI)
	2%	GEMS/Food G06	2.01	2%	Wheat	0.0%	Sugar beet roots	0.0%	Beetroots		
	2%	IT toddler	2.88	2%	Wheat		Grapefruits				
	1%	RO general	2.12	1%	Wheat	0.0%	Sugar beet roots	0.0%	Beetroots		
	1%	NL child	2.10	1%	Wheat	0.3%	Sugar beet roots	0.0%	Rapeseeds/canola seeds		
	1%	FR child 3-15 yr	2.05	1%	Wheat	0.1%	Sugar beet roots	0.0%	Beetroots		
	1%	NL toddler	1.88	1%	Wheat	0.2%	Sugar beet roots	0.0%	Rapeseeds/canola seeds		
	1%	GEMS/Food G15	1.85	1%	Wheat	0.0%	Beetroots	0.0%	Rapeseeds/canola seeds		
	1%	ES child	1.81	1%	Wheat	0.0%	Sugar beet roots	0.0%	Beetroots		
	1%	DK child	1.79	1%	Wheat	0.0%	Beetroots	0.0%	Rapeseeds/canola seeds		
	1%	UK toddler	1.75	1%	Wheat	0.1%	Sugar beet roots	0.0%	Beetroots		
	1%	GEMS/Food G07	1.72	1%	Wheat	0.0%	Beetroots	0.0%	Rapeseeds/canola seeds		
	1%	DE child	1.70	1%	Wheat	0.0%	Beetroots	0.0%	Rapeseeds/canola seeds		
	1%	IT adult	1.68	1%	Wheat	0.0%	Beetroots	0.0%	Rapeseeds/canola seeds		
	1%	GEMS/Food G08	1.66	1%	Wheat	0.0%	Beetroots	0.0%	Rapeseeds/canola seeds		
	1%	GEMS/Food G10	1.50	1%	Wheat	0.0%	Beetroots	0.0%	Rapeseeds/canola seeds		
	1%	PT general	1.59	1%	Wheat		Grapefruits				
	1.0%	GEMS/Food G11	1.46	1.0%	Wheat	0.0%	Beetroots				
	0.9%	FR toddler 2-3 yr	1.35	0.8%	Wheat	0.1%	Sugar beet roots	0.0%	Beetroots		
	0.9%	SE general	1.30	0.9%	Wheat	0.0%	Beetroots				
	0.8%	UK infant	1.15	0.7%	Wheat	0.0%	Sugar beet roots				
	0.7%	DE women 14-50 yr	1.10	0.6%	Wheat	0.2%	Sugar beet roots	0.0%	Beetroots		
	0.7%	DE general	0.98	0.5%	Wheat	0.1%	Sugar beet roots	0.0%	Beetroots		
	0.6%	ES adult	0.96	0.6%	Wheat	0.0%	Sugar beet roots	0.0%	Beetroots		
	0.6%	FR adult	0.94	0.6%	Wheat	0.0%	Sugar beet roots	0.0%	Beetroots		
	0.6%	E adult	0.84	0.6%	Wheat	0.0%	Beetroots				
	0.6%	NL general	0.83	0.5%	Wheat	0.1%	Sugar beet roots	0.0%	Rapeseeds/canola seeds		
	0.6%	UK vegetarian	0.86	0.6%	Wheat	0.0%	Sugar beet roots	0.0%	Beetroots		
	0.5%	UK adult	0.71	0.5%	Wheat	0.0%	Sugar beet roots	0.0%	Beetroots		
	0.3%	FI 3 yr	0.48	0.3%	Wheat	0.0%	Beetroots	0.0%	Rapeseeds/canola seeds		
	0.3%	E child	0.47	0.3%	Wheat	0.0%	Beetroots				
	0.3%	DK adult	0.46	0.3%	Wheat		Grapefruits				
	0.3%	LT adult	0.45	0.3%	Wheat	0.0%	Beetroots	0.0%	Beetroots		
	0.3%	FI 6 yr	0.40	0.3%	Wheat	0.0%	Beetroots		Rapeseeds/canola seeds		
	0.3%	FR infant	0.39	0.2%	Wheat	0.0%	Sugar beet roots	0.0%	Beetroots		
	0.1%	FI adult	0.15	0.1%	Wheat	0.0%	Beetroots	0.0%	Rapeseeds/canola seeds		
	0.0%	PL general	0.01	0.0%	Beetroots		Grapefruits				

## A 3.1 IESTI calculations - Raw commodities

Acute risk assessment / children				Acute risk assessment / adults / general population				Acute risk assessment / children				Acute risk assessment / adults / general population				
Details - acute risk assessment / children				Details - acute risk assessment / adults				Hide IESTI new calculations				Show IESTI new calculations				
The acute risk assessment is based on the ARID. The calculation is based on the large portion of the most critical consumer group.								ESTI new calculations: The calculation is performed with the MRL and the peeling/processing factor (PF), taking into account the residue in the edible portion and/or the conversion factor for the residue definition (CF). For case 2a, 2b and 3 calculations a variability factor of 3 is used. Since this methodology is not based on internationally agreed principles, the results are considered as indicative only. Since this methodology is not based on internationally agreed principles, the results are considered as indicative only.								
Show results of IESTI calculation for all crops																
Unprocessed commodities	Results for children No. of commodities for which ARID/ADI is exceeded (ESTI): ---				Results for adults No. of commodities for which ARID/ADI is exceeded (ESTI): ---				ESTI new Results for children No. of commodities for which ARID/ADI is exceeded (ESTI new): ---				ESTI new Results for adults No. of commodities for which ARID/ADI is exceeded (ESTI new): ---			
	ESTI				ESTI				ESTI new				ESTI new			
	Highest % of ARID/ADI	Commodities	MRL / input for RA (µg/kg bw)	Exposure (µg/kg bw)	Highest % of ARID/ADI	Commodities	MRL / input for RA (µg/kg bw)	Exposure (µg/kg bw)	Highest % of ARID/ADI	Commodities	MRL / input for RA (µg/kg bw)	Exposure (µg/kg bw)	Highest % of ARID/ADI	Commodities	MRL / input for RA (µg/kg bw)	Exposure (µg/kg bw)
	6%	Wheat	3 / 0.7	10	3%	Wheat	3 / 0.7	5.9	25%	Wheat	3 / 3	43	15%	Wheat	3 / 3	25
	0.02%	Rapeseeds/canola seeds	0.5 / 0.03	0.03	0.01%	Rapeseeds/canola seeds	0.5 / 0.03	0.01	0.4%	Rapeseeds/canola seeds	0.5 / 0.5	0.69	0.2%	Rapeseeds/canola seeds	0.5 / 0.5	0.26
Expand/collapse list																
Total number of commodities exceeding the ARID/ADI in children and adult diets (ESTI calculation)								Total number of commodities found exceeding the ARID/ADI in children and adult diets (ESTI new calculation)								
Processed commodities	Results for children No. of processed commodities for which ARID/ADI is exceeded (ESTI): ---				Results for adults No. of processed commodities for which ARID/ADI is exceeded (ESTI): ---				ESTI new Results for children No. of processed commodities for which ARID/ADI is exceeded (ESTI new): ---				ESTI new Results for adults No. of processed commodities for which ARID/ADI is exceeded (ESTI new): ---			
	ESTI				ESTI				ESTI new				ESTI new			
	Highest % of ARID/ADI	Processed commodities	MRL / input for RA (mg/kg)	Exposure (µg/kg bw)	Highest % of ARID/ADI	Processed commodities	MRL / input for RA (mg/kg)	Exposure (µg/kg bw)	Highest % of ARID/ADI	Processed commodities	MRL / input for RA (mg/kg)	Exposure (µg/kg bw)	Highest % of ARID/ADI	Processed commodities	MRL / input for RA (mg/kg)	Exposure (µg/kg bw)
	21%	Sugar beets (root) / sugar	1 / 3.84	35	8%	Sugar beets (root) / sugar	1 / 3.84	14	65%	Sugar beets (root) / sugar	1 / 12	110	26%	Sugar beets (root) / sugar	1 / 12	44
	5%	Wheat / milling (flour)	3 / 0.7	8.5	2%	Wheat / bread/pizza	3 / 0.7	3.1	21%	Wheat / milling (flour)	3 / 3	36	8%	Wheat / bread/pizza	3 / 3	13
	2%	Wheat / milling (wholemeal)	3 / 0.7	3.9	2%	Wheat / pasta	3 / 0.7	2.7	10%	Wheat / milling (wholemeal)	3 / 3	17	7%	Wheat / pasta	3 / 3	11
	0.0%	Rapeseeds / oils	0.5 / 0.05	0.01	1%	Wheat / bread (wholemeal)	3 / 0.7	2.4	0.2%	Rapeseeds / oils	0.5 / 1	0.29	6%	Wheat / bread (wholemeal)	3 / 3	10
	ILICZBAI	ILICZBAI	ILICZBAI	ILICZBAI	ILICZBAI	ILICZBAI	ILICZBAI	ILICZBAI	ILICZBAI	ILICZBAI	ILICZBAI	ILICZBAI	ILICZBAI	ILICZBAI	ILICZBAI	ILICZBAI
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Expand/collapse list																

New calculations:

### A 3.2 IESTI calculations - Processed commodities

## New calculations:

[illegible]

