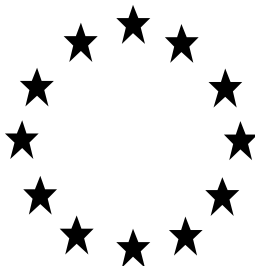


Draft Renewal Assessment Report
under Regulation (EC) 1107/2009



CLOPYRALID

Volume 3 – B.5 (PPP) – GF-1374

RMS: Finland
Co-RMS: Poland

May 2017

Volume 1

Level 1: Statement of subject matter and purpose for which this report has been prepared and background information on the application

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Annex B.7 (PPP): Residue data

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Annex C: Confidential information and, where relevant, details of any task force formed for the purpose of generating tests and studies submitted

List of Endpoints

Version History

When	What
2017/May	DRAR- First version submitted to EFSA

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B.5. METHODS OF ANALYSIS

The representative formulation includes a **different product (GF-1374) compared to the product evaluated for the first approval** (Lontrel 100 Herbicide). GF-1374 is an emulsifiable concentrate containing the active substance clopyralid at 80 g ae/l and 2 mixing partners namely Fluroxypyr meptyl 144 g/l (100 g ae/L) and Florasulam 2.5 g/l.

B.5.1. METHODS USED FOR THE GENERATION OF PRE-AUTHORISATION DATA

B.5.1.1. Analysis of the plant protection product

GF-1374 was not the representative formulation for the Active Approval of Clopyralid.

Data to address this point was not evaluated as part of the Active Approval therefore all relevant data are provided.

Report:	CP 5.1.1/01 , Cathie, C.A. (2005) Analytical Method Used for Studies Submitted Under : CP 2.1/1, CP 2.3/1, CP 2.4/1, CP 2.4/2, CP 2.5/1, CP 2.5/2, CP 2.6/1, CP 2.7/1, CP 2.7/2, CP 2.8.2/1 and CP 2.8.6/1 (Study ID 05-683-G) CP 2.7/1 (Study ID NAFST-13-163) CP 2.7/1, CP 2.8.2/1 and CP 2.8.6/1 (Study ID 05-676-G) CP 2.7/3 and CP 2.8.2/1 (Study ID 05-678-G) CP 2.7/3 (Study ID NAFST-13-164.01)
Title:	Validation of a Method for the Determination of Clopyralid, Florasulam and Fluroxypyr meptyl in GF-1374
Document No:	DAS-AM-05-004
Guidelines:	Not stated
GLP	Yes

Description of the method	The method is an internal standard HPLC method using a Zorbax RX C8 column (250 × 4.6 mm, 5 µm) and UV detection at 240 nm.
Specificity	The method is capable of and was validated for determining clopyralid, florasulam and fluroxypyr meptyl in the presence of each other. Retention times for clopyralid, florasulam and fluroxypyr meptyl in the gradient mobile phase method are approximately 3.7, 10.5, and 31.2 minutes respectively.
Interference by other substances	There are no interferences from any of the components present in the formulation. This was confirmed by separately analysing the formulation inerts, clopyralid technical, florasulam technical, fluroxypyr meptyl technical and the internal standard.

Linearity	<p>The linearity for clopyralid was tested from 289 to 1191 µg/mL (3.9% w/w to 15.9% w/w) at the conditions described earlier. The coefficient of determination (r^2) was determined to be 0.99986. The equation from the regression analysis was $y = 4.74 x$ (intercept = 0).</p> <p>The linearity for florasulam was tested from 10.2 to 40.9 µg/mL (0.14% w/w to 0.55% w/w) at the conditions described earlier. The coefficient of determination (r^2) was determined to be 0.99994. The equation from the regression analysis was $y = 8.19 x$ (intercept = 0).</p> <p>The linearity for fluroxypyr meptyl was tested from 507 to 2026 µg/mL (6.8% w/w to 27.0 % w/w) at the conditions described earlier. The coefficient of determination (r^2) was determined to be 0.99991. The equation from the regression analysis was $y = 8.38 x$ (intercept = 0).</p>
Accuracy	<p>The accuracy of the method was tested through the preparation of synthetic samples at a range of concentrations. Recovery of clopyralid ranged from 99.2 % to 102.5% at concentrations ranging from 5.4% w/w to 9.6% w/w. Recovery of florasulam ranged from 97.3% to 103.7% at concentrations ranging from 0.18% w/w to 0.32% w/w. Recovery of fluroxypyr meptyl ranged from 99.0% to 100.9% at concentrations ranging from 9.9% w/w to 17.3% w/w.</p>
Repeatability	<p>The method precision was determined by preparing 5 separate samples on each of 2 days and determining the amount of clopyralid, florasulam, and fluroxypyr meptyl in each of them. The relative standard deviation (%RSD) was determined to be 0.41% for clopyralid, 1.31% for florasulam, and 0.21% for fluroxypyr meptyl. Precision of clopyralid at 95% confidence was $\pm 0.9\%$ at an average concentration of 7.67% w/w. Precision of florasulam at 95% confidence was $\pm 3.0\%$ at an average concentration of 0.248% w/w. Precision of fluroxypyr meptyl at 95% confidence was $\pm 0.5\%$ at an average concentration of 13.28% w/w. No outliers were discarded during calculation of the relative standard deviation.</p>
Applicability of existing CIPAC methods	No CIPAC method is available

Study Comments: 5.1.1/01	<p>Specificity: No interferences</p> <p>Linearity: Linear over the respective concentration ranges for clopyralid, florasulam and fluroxypyr meptyl (7 different concentrations) Coefficient of determination $r^2 > 0.9998$</p> <p>Precision: $RSD = 0.21-1.31 \% < \text{Horwitz } RSD_r$ (clopyralid, florasulam and fluroxypyr meptyl)</p> <p>Accuracy: Mean recovery 99.9 – 100.8 % (clopyralid, florasulam and fluroxypyr meptyl)</p> <p>HPLC was employed for the determination of the active substances clopyralid, florasulam and fluroxypyr meptyl in the formulation GF-1374.</p> <p>The validation is acceptable, and the method is suitable for the determination of the active substances clopyralid, florasulam and fluroxypyr meptyl in the formulation GF-1374.</p>
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Agreed endpoint: 5.1.1/01	HPLC-UV
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B.5.1.1.1. Methods for determination of relevant impurities identified in the technical material or which may be formed during manufacture of the plant protection product or from degradation of the plant protection product during storage

Relevant impurities

There are no relevant impurities in GF-1374, therefore no analytical method is required.

B.5.1.1.2 .Methods for the determination of relevant co-formulants or components of co formulants, where required by the national competent authorities

No methods are required as none of the co-formulants are defined as relevant for toxicity (environment, health).

B.5.1.2. Methods for the determination of residues

See Volume 3- B.5 (AS).

Rationale for Submission of Analytical Summaries for Data Generation Methods:

Analytical methods used for the generation of pre-approval data are summarized below. Only analytical methods that quantitated clopyralid and were used in non-isotope labelled studies not previously reviewed and accepted by the RMS and EFSA, were summarized and compiled. The analytical method summaries include the recovery, precision, limit of quantitation, specificity and linearity of the method as outlined in SANCO/3029/99 rev.4 for validation of a data generation method.

Table 5.1.2-1 – Summary of Validated Methods for the Generation of Pre-Authorization Data

Matrix type	Method LOQ	Principle of method (i.e. GC-MS or HPLC-UV)	Author(s), year / missing / EU agreed
Environmental Fate (CP 5.1.2(a))			
Efficacy (CP 5.1.2(b))			
-	-		-
Toxicology (CP 5.1.2(c))			
-	-		-
Exposure (CP 5.1.2(d))			
-	-		-
Residues (CP 5.1.2(e))			

Matrix type	Method LOQ	Principle of method (i.e. GC-MS or HPLC-UV)	Author(s), year / missing / EU agreed
Ecotoxicology (CP 5.1.2(f))			
Spray Solution	18.04 mg/L	LC-UV	CP 5.1.2(f)/1 Eley, R.(2008) Used for study: EA05B2A033 Submitted under: CP 10.6.2/1
Spray Solution	18.04 mg/L	LC-UV	CP 5.1.2(f)/2 Eley, R.(2008) Used for study: EA05B2A020 Submitted under: CP 10.6.2/2
Physical and Chemical Properties (CP 5.1.2 (g))			
Formulation GF-1374	289 µg/mL	LC-UV	CP 5.1.1/01 Cathie, C.(2005) Used for studies: 05-683-G, NAFST-13-163, 05-676-G, 05-678-G and NAFST-13-164.01 Submitted under: CP 2.1/1, CP 2.3/1, CP 2.4/1, CP 2.4/2, CP 2.5/1, CP 2.5/2, CP 2.6/1, CP 2.7/1, CP 2.7/2, CP 2.8.2/1 and CP 2.8.6/1 (Study ID 05-683-G) CP 2.7/1 (Study ID NAFST-13-163) CP 2.7/1, CP 2.8.2/1 and CP 2.8.6/1 (Study ID 05-676-G) CP 2.7/3 and CP 2.8.2/1 (Study ID 05-678-G) CP 2.7/3 (Study ID NAFST-13-164.01)

CP 5.1.1 (a) Methods in soil, water, sediment, air and any additional matrices used in support of environmental fate studies

No new studies were submitted that monitored clopyralid and were non-radiolabelled.

CP 5.1.1 (b) Methods in soil, water and any additional matrices used in support of efficacy studies

See Point 5.2 (c) (soil) and Point 5.2 (d) (water). No new studies were submitted that monitored clopyralid and were non-radiolabelled.

CP 5.1.1 (c) Methods in feed, body fluids and tissues, air and any additional matrices used in support of toxicological studies

See Point 5.2 (a) (feed), Point 5.2 (b) (body fluids and tissues) and Point 5.2 (e) (air). No new studies were submitted that monitored clopyralid and were non-radiolabelled.

CP 5.1.1 (d) Methods in body fluids, air and any additional matrices used in support of operator, worker, resident and bystander exposure studies

See Point 5.2 (b) (body fluids) and Point 5.2 (e) (air). No new studies were submitted that monitored clopyralid and were non-radiolabelled.

CP 5.1.1 (e) Methods in or on plants, plant products, processed food commodities, food of plant and animal origin, feed and any additional matrices used in support of residues studies

See Point 5.2 (a) (plants, plant products, processed food commodities, food of plant and animal origin, feed). No new studies were submitted that monitored clopyralid and were non-radiolabelled.

CP 5.1.1 (f) Methods in soil, water, sediment, feed and any additional matrices used in support of ecotoxicology studies

See Point 5.2 (c) (soil) and Point 5.2 (d) (water, sediment) and Point 5.2 (a) (plants, plant products, processed food commodities, food of plant and animal origin, feed).

Report	CP 5.1.2(f)/1 Eley,R. (amendment 2008; original 2005) (analytical report performed by Comb, 2005) Study submitted under CP 10.6.2/1 (EA05B2A033)
Title	Evaluation of the Phytotoxicity of GF-1374 (Fluroxypyr-1-MHE + Clopyralid + Florasulam, EC) GLP Vegetative Vigour Test - Terrestrial Non Target Plants (Based on OECD Guideline 208 B) Additional information: Assessment of the analytical method
Study ID	AgroChemex Study Number: ACE-05-152 Dow AgroSciences Study Number: EA05B2A033
Performing Laboratory	AgroChemex Ltd., Aldhams Farm, Manningtree, C011 2NF, UK. Analytical report performed in Huntingdon Life Sciences Ltd., Woolley Road, Alconbury, Huntingdon, Cambridgeshire, PE28 4HS, England
Guidelines	SANCO/3029/99 rev. 4
GLP	Yes
Method Principle	The contents of the active ingredients, fluroxypyr-meptyl, clopyralid and florasulam, in the spray solutions were determined using a high performance liquid chromatography (HPLC) method with UV detection.

	<p>Prior to HPLC analysis, the samples were sonicated for 20 minutes to ensure homogeneity and were then stirred for 5 minutes prior to sampling. The stirring was continued as aliquots were removed for analysis.</p> <p>Triplicate samples of the supplied spray solutions were pipetted into separate volumetric flasks and diluted to volume with methanol. The resulting solutions were filtered prior to analysis by the HPLC/UV method relative to the bracketing standard solution.</p> <p>Equipment/conditions:</p> <p>Hewlett Packard LC/UV, wavelength 240 nm</p> <p>LC Column: Zorbax RX-C8, 25 cm x 4.6 mm</p> <p>Mobile phase: 0.179% w/v aqueous potassium dihydrogen phosphate:methanol (7:3 v/v), adjusted to pH 3.8 and and methanol; gradient elution.</p>																
Recovery	<p>The validity of the method was proven by determination of clopyralid in three spray solutions. The mean recoveries were in the range of 70 – 110% at each fortification level.</p> <p>Table 1. Recovery of Clopyralid in Spray Solutions</p> <table><tr><th>Theoretical Concentration (mg/L)</th><th>Mean Recovery %</th><th>% RSD</th><th>N</th></tr><tr><td>590.8</td><td>101</td><td>16.8</td><td>3</td></tr><tr><td>623.6</td><td>92</td><td>18.6</td><td>3</td></tr><tr><td>588.7</td><td>93</td><td>3.14</td><td>3</td></tr></table>	Theoretical Concentration (mg/L)	Mean Recovery %	% RSD	N	590.8	101	16.8	3	623.6	92	18.6	3	588.7	93	3.14	3
Theoretical Concentration (mg/L)	Mean Recovery %	% RSD	N														
590.8	101	16.8	3														
623.6	92	18.6	3														
588.7	93	3.14	3														
Repeatability	Relative standard deviations at each fortification level were below the 20% criterion, demonstrating good repeatability of the method.																
Specificity	The method is specific for the determination of clopyralid by virtue of the chromatographic separation and detection system used.																
Limit of Quantitation	18.04 mg/L																
Linearity	Calibration curves were calculated using linear regression forced through zero, with 5 data points over the concentration of 18.04 to 90.22 mg/L with a correlation coefficient of 0.9957.																

Study Comments: 5.1.2(f)/1	According to SANCO/3029/99 rev. 4, 5 determinations should be made at each fortification level. Although this criteria is not quite fulfilled, the method and the LOQ can be considered to be fit for purpose.
Agreed endpoint: 5.1.2(f)/1	HPLC-UV

Report	<p>CP 5.1.2(f)/2</p> <p>Eley,R. (amendment 2008; original 2005) (analytical report performed by Comb, 2005)</p> <p>Study submitted under CP 10.6.2/2 (EA05B2A020)</p>
Title	<p>Evaluation of the Phytotoxicity of GF-1374 (Fluroxypyr-1-MHE + Clopyralid + Florasulam, 144+80+2.5 g as/l, EC) GLP Seedling Emergence and Seedline Growth Test - Based on OECD Guideline 208 A)</p> <p>Additional information: Assessment of the analytical method</p>
Study ID	<p>AgroChemex Study Number: ACE-05-151</p> <p>Dow AgroSciences Study Number: EA05B2A020</p>
Performing Laboratory	<p>AgroChemex Ltd., Aldhams Farm, Manningtree, C011 2NF, UK.</p> <p>Analytical report performed in Huntingdon Life Sciences Ltd., Woolley Road, Alconbury, Huntingdon, Cambridgeshire, PE28 4HS, England</p>
Guidelines	SANCO/3029/99 rev. 4
GLP	Yes
Method Principle	<p>The contents of the active ingredients, fluroxypyr-meptyl, clopyralid and florasulam, in the spray solutions were determined using a high performance liquid chromatography (HPLC) method with UV detection.</p> <p>Prior to HPLC analysis, the samples were sonicated for 20 minutes to ensure homogeneity and were then stirred for 5 minutes prior to sampling. The stirring was continued as aliquots were removed for analysis.</p> <p>Triplicate samples of the supplied spray solutions were pipetted into separate volumetric flasks and diluted to volume with methanol. The resulting solutions were filtered prior to analysis by the HPLC/UV method relative to the bracketing standard solution.</p> <p>Equipment/conditions:</p> <p>Hewlett Packard LC/UV, wavelength 240 nm</p> <p>LC Column: Zorbax RX-C8, 25 cm x 4.6 mm</p> <p>Mobile phase: 0.179% w/v aqueous potassium dihydrogen phosphate:methanol (7:3 v/v), adjusted to pH 3.8 and and methanol; gradient elution.</p>

Recovery	<p>The validity of the method was proven by determination of clopyralid in two spray solutions. The mean recoveries were in the range of 70 – 110% at each fortification level.</p> <p>Table 1. Recovery of Clopyralid in Spray Solutions</p> <table><tr><th>Theoretical Concentration (mg/L)</th><th>Mean Recovery %</th><th>% RSD</th><th>n</th></tr><tr><td>601.3</td><td>103</td><td>4.08</td><td>3</td></tr><tr><td>600.3</td><td>96</td><td>1.71</td><td>3</td></tr></table>	Theoretical Concentration (mg/L)	Mean Recovery %	% RSD	n	601.3	103	4.08	3	600.3	96	1.71	3
Theoretical Concentration (mg/L)	Mean Recovery %	% RSD	n										
601.3	103	4.08	3										
600.3	96	1.71	3										
Repeatability	Relative standard deviations at each fortification level were below the 20% criterion, demonstrating good repeatability of the method.												
Specificity	The method is specific for the determination of clopyralid by virtue of the chromatographic separation and detection system used.												
Limit of Quantitation	18.04 mg/L.												
Linearity	Calibration curves were calculated using linear regression forced through zero, with 5 data points over the concentration of 18.04 to 90.22 mg/L with a correlation coefficient of 0.9957.												
Conclusion	Due to the simplicity of the method, the validation was accepted even though the number of replicates was not n=5 as specified in SANCO 3029.												

Study Comments: 5.1.2(f)/2	According to SANCO/3029/99 rev. 4, 5 determinations should be made at each fortification level. Although this criteria is not quite fulfilled, the method and the LOQ can be considered to be fit for purpose.
Agreed endpoint: 5.1.2(f)/2	HPLC-UV

CP 5.1.1 (g) Methods in water, buffer solutions, organic solvents and any additional matrices resulting from the physical and chemical properties tests

The validation can be found in the individual reports of the physical properties testing.

See also [CP 5.1.1/01](#), Cathie, C.A. (2005)

B.5.2. METHODS FOR POST-APPROVAL CONTROL AND MONITORING PURPOSES**B.5.2.1 Methods for the determination of residues in or on plants, plant products, processed food commodities, food and feed of plant and animal origin****Crop Matrices****Clopyralid**

Methods for the determination of clopyralid residues in plants, plant products, processed food commodities and animal products have been described in **Volume 3- B.5 (AS)**, Point 4.2 (a) and the crop methods are summarised in **Table 5.2(a)-01**. Picloram is included in the method validation summary since both picloram and clopyralid were validated in the same method due to their similarity in structure.

Table 5.2(a)-01: EU Conclusions: Analytical methods for residues of clopyralid in crops

Crop/Matrix	EU Agreed Method ¹			Proposed Method ²			
	Method	Analyte	LOQ (mg/kg)	Method	Analyte	LOQ (mg/kg)	Reference
<u>Dry Crops:</u> Wheat Grain <u>Wet Crops:</u> Wheat Forage <u>Acidic Crops:</u> Orange <u>Oily Crops:</u> Oilseed Rape Seeds				LC-MS/MS	Clopyralid and Picloram	0.01	DAS 120610, Vogl, E.; 2012 (Validation)
<u>Wet Crops:</u> Wheat Whole Plant <u>Oily Crops:</u> Oilseed Rape Seeds				LC-MS/MS	Clopyralid and Picloram	0.01	DAS 120614, Austin, R., 2012 (ILV)

² New methods that comply with SANCO 825/00 rev 8.1 have been submitted as part of the Annex I renewal of clopyralid.

Florasulam

Analytical methods are active substance data and were provided in the EU review of florasulam and **were considered adequate**. The current methods available for the determination of residues of florasulam in crops are summarised in **Table 5.2(a)-02**. Since active substance renewal, no new methods have been submitted.

Table 5.2(a)-02: EU Conclusions: Analytical methods for residues of florasulam in crops

Crop/Matrix	EU Agreed Method ¹			Proposed Method ²			
	Method	Analyte	LOQ (mg/kg)	Method	Analyte	LOQ (mg/kg)	Reference
Acidic crops Dry Crops Oily Crops Wet Crops	LC-MS/MS	Florasulam	0.01	-	-	-	-

¹ Report EFSA Journal 2015;13(1):3984

² Since active substance renewal, no new methods have been submitted.

Fluroxypyr-meptyl

All analytical methods are active substance data and were provided in the EU review of fluroxypyr (fluroxypyr-meptyl) and **were considered adequate**. Details of the EU agreed methods for determination of fluroxypyr-meptyl residues in crops are provided below in **Table 5.2(a)-03**. **Since Annex I inclusion, new methods have been developed** to incorporate the use of LC-MS/MS and a full summary of the method validation is provided below. However, **they have not been accessed in this context**.

Table 5.2(a)-03: EU conclusions: Analytical methods for residues of fluroxypyr-meptyl in crops

Crop/ Matrix	EU agreed method ¹			Proposed method ²			
	Method	Analyte	LOQ (mg/kg)	Method	Analyte	LOQ (mg/kg)	Reference
Hay Wheat Barley Oats	GC-MS/MS	Fluroxypyr and its salts, esters and conjugates expressed as fluroxypyr.	0.01 (grain) 0.05 (forage, straw and hay)	-	-	-	-
Wet Crops, Dry Crops, Oily Crops, Acidic Crops Bovine Milk	-	-	-	LC-MS/MS	Fluroxypyr 1-methylheptyl Ester (as the acid equivalent)	0.01	DAS 091171, ██████████ 2010 (Validation)
Wet Crops, Dry Crops, Oily Crops, Acidic Crops Bovine Milk				LC-MS/MS	Fluroxypyr 1-methylheptyl Ester (as the acid equivalent)	0.01	DAS 101082, ██████████ 2010 (ILV)

¹ Report EFSA Journal 2011; 9(3); 2091² Since Annex I inclusion, new methods have been developed and a full study summary is provided below in support of this application.

The following residue analytical studies on agricultural commodities (wet crops, dry crops, acidic crops, oily crops) have not previously been reviewed and are provided in support of this assessment. However, **as they are active substance data, they have not been accessed in this context.**

Method Validation for the Determination of Fluroxypyr 1-methylheptyl Ester as the Acid Equivalent in Crop Matrices

Report:	██████████ (2010a)
Title:	Validation Report for the Determination of Residues of Fluroxypyr 1-methylheptyl Ester as the Acid Equivalent in Agricultural Commodities and Fluroxypyr in Bovine Milk by High Performance Liquid Chromatography with Tandem Mass Spectrometry
Document No:	Method Validation Report Number 091171
Guidelines:	OPPTS 850.7100 SANCO/3029/00 rev.4 SANCO/825/00 rev 7 Dir98-02
GLP	Yes
Matrix, limit of determination	0.01 µg/g (mg/kg) for all matrices
Description	<p>Summary of technique:</p> <p>Residues of fluroxypyr 1-MHE and fluroxypyr are extracted from agricultural commodities (wet crops, dry crops, acidic crops, oily crops) by homogenizing with an acetone/0.25 N hydrochloric acid (60:40) solution. The sample is shaken and centrifuged. An aliquot of the sample is taken and placed in 12 mL culture tube, and fluroxypyr 1-MHE is hydrolysed to fluroxypyr by adding 50 µL of a 5.0 N sodium hydroxide solution. Acetone is evaporated from the sample under a steam of nitrogen on a TurboVap set at 40 °C. A 1.0-mL aliquot of 5.0 N hydrochloric acid is added to the sample. The sample tube is capped and placed in an oven a set at 90 °C for approximately two hours. This step allows the sample to hydrolyse releasing any fluroxypyr conjugates. An 8 mL aliquot of HPLC grade water is added to the sample tube, and the sample is vortex mixed. The sample is loaded onto a Strata X polymeric sorbent SPE column for purification and concentration. The column is conditioned and the sample is loaded. The column is then washed with two 750 µL aliquots of an acetonitrile/0.1 N hydrochloric acid (20:80) solution and then dried under full vacuum for about 20 minutes. Fluroxypyr is eluted from the SPE column with two 500 µL aliquots of acetonitrile/0.1 N hydrochloric acid (60:40). A 50 µL aliquot of the 0.5 µg/mL internal standard solution is added to the sample, and the sample is analysed by liquid chromatography with negative-ion electrospray ionization (ESI) tandem mass spectrometry (LC/MS/MS).</p>
Specificity	<p>The method is highly selective for the determination of fluroxypyr 1-MHE (determined as the fluroxypyr acid equivalent) in agricultural commodities and for the determination of fluroxypyr in bovine milk products by virtue of the chromatographic separation and selective detection system used. To demonstrate further confirmation, additional fluroxypyr ion transitions can be monitored as follows:</p> <p>Q1/Q3 <i>m/z</i> 252.9/232.8 (quantification)</p> <p>Q1/Q3 <i>m/z</i> 252.9/194.9 (confirmation)</p>

Linearity	For the linear regression analysis describing the detector response as a function of the standard calibration curve concentrations, the coefficients of determination (r ²) were all equal to or greater than 0.99 for all of the quantitative calibration curve determinations during the method validation study. The results indicate linearity of the detector response as a function of the standard concentration.				
Accuracy	The average recoveries for fluroxypyr in all of the agricultural commodities were between 70 and 110% with the exception of oily crops. Typical recoveries for fluroxypyr in oily crops ranged from 58% and 84% with an overall average recovery of fluroxypyr from oily crops of 66% for the quantification transition. While the overall and individual recoveries of fluroxypyr in oily crops were not between the required range (70-110%) according to the current guidelines, SANCO/825/00, they were very consistent with low relative standard deviations and therefore considered acceptable.				
Repeatability	The relative standard deviations (RSDs) obtained at each fortification level were in the range of 2.7% to 11.3%. Results obtained were within guideline requirements (RSD ≤ 20%).				
Reproducibility	An independent laboratory validation was conducted and is presented below.				
Validation Data					
Matrices	Fortification Level (mg/kg)	Recovery Rate (%)		% RSD	n
		Mean	Range		
Quantification Transition Q1/Q3 <i>m/z</i> 252.9/232.8					
Acidic crops	0.01	85	72-96	10.2	12
	0.10	90	83-101	7.5	6
	1.00	88	82-92	3.6	10
	Overall	87	72-101	7.8	28
Dry crops	0.01	80	67-99	11.3	12
	0.10	88	78-96	7.6	6
	1.00	86	82-88	2.8	5
	Overall	83	67-99	9.9	23
Oily crops	0.01	67	61-84	9.8	11
	0.10	64	58-73	7.5	6
	1.00	66	62-72	4.8	10
	Overall	66	58-84	7.6	27
Wet crops	0.01	84	72-98	10.9	9
	0.10	92	81-100	6.2	9
	1.00	84	79-90	4.8	5
	Overall	87	72-100	8.9	23
Bovine Milk	0.01	91	78-100	5.6	14
	0.10	94	85-100	4.9	7

	1.00	91	87-96	2.7	11
	Overall	92	78-100	4.6	32
Confirmatory Transition Q1/Q3 m/z 252.9/194.9					
Acidic crops	0.01	79	65-100	15.1	12
	0.10	91	87-96	3.5	6
	1.00	88	80-92	4.5	10
	Overall	85	65-100	11.2	28
Dry crops	0.01	80	65-111	16.1	12
	0.10	90	81-108	10.4	6
	1.00	93	91-96	2.2	5
	Overall	85	65-111	13.7	23
Oily crops	0.01	67	52-75	10.1	11
	0.10	68	64-75	6.4	6
	1.00	70	64-78	6.8	10
	Overall	68	52-78	8.2	27
Wet crops	0.01	85	79-94	5.9	9
	0.10	92	83-100	7.2	9
	1.00	87	81-91	4.1	5
	Overall	88	79-100	7.0	23
Bovine Milk	0.01	87	81-96	6.7	14
	0.10	91	86-96	4.0	7
	1.00	94	90-99	2.8	11
	Overall	90	81-99	5.9	32

Independent Laboratory Validation of the Enforcement Method for the Determination of Fluroxypyr 1-methylheptyl Ester as the Acid Equivalent in Crop Matrices

Report:	██████████ (2010a)
Title:	Independent Laboratory Validation of a Method for the Determination of Residues of Fluroxypyr 1-methylheptyl Ester as the Acid Equivalent in Agricultural Commodities and Bovine Milk
Document No:	Dow AgroSciences Study Reference No.: 101082 CEMAS Study No.: CEMS-4625
Guidelines:	OECD Principles of Good Laboratory Practice UK Good Laboratory Practice Regulations 1999 (S.I. 1999/3106, as amended by S.I. 994, 2004) OPPTS 850.7100 SANCO/3029/00 rev.4 SANCO/825/00 rev 7 Dir98-02
GLP	Yes
Matrix, limit of determination	0.01 µg/g (mg/kg) for all matrices
Description	Summary of technique:

	<p>Residues of fluroxypyr 1-MHE and fluroxypyr are extracted from agricultural commodities (wet crops, dry crops, acidic crops, oily crops) by homogenizing with an acetone/0.25 N hydrochloric acid (60:40) solution. The sample is shaken and centrifuged. An aliquot of the sample is taken and placed in 12 mL culture tube, and fluroxypyr 1-MHE is hydrolysed to fluroxypyr by adding 50 μL of a 5.0 N sodium hydroxide solution. Acetone is evaporated from the sample under a stream of nitrogen on a TurboVap set at 40 °C. A 1.0 mL aliquot of 5.0 N hydrochloric acid is added to the sample. The sample tube is capped and placed in an oven set at 90 °C for approximately two hours. This step allows the sample to hydrolyse releasing any fluroxypyr conjugates. An 8 mL aliquot of HPLC grade water is added to the sample tube and the sample is vortex mixed. The sample is loaded onto a Strata -X polymeric sorbent SPE column for purification and concentration. The column is conditioned and the sample is loaded. The column is then washed with two 750 μL aliquots of an acetonitrile/0.1 N hydrochloric acid (20:80) solution and then dried under full vacuum for about 20 minutes. Fluroxypyr is eluted from the SPE column with two 500 μL aliquots of acetonitrile/0.1 N hydrochloric acid (60:40). A 50 μL aliquot of the 0.5 μg/mL internal standard solution is added to the sample and the sample is analysed by liquid chromatography with negative-ion electrospray ionization (ESI) tandem mass spectrometry (LC/MS/MS).</p>
Specificity	<p>The method is highly selective for the determination of fluroxypyr 1-MHE (determined as the fluroxypyr acid equivalent) in agricultural commodities and for the determination of fluroxypyr in bovine milk products by virtue of the chromatographic separation and selective detection system used. To demonstrate further confirmation, additional fluroxypyr ion transitions can be monitored as follows:</p> <p>Fluroxypyr Q1/Q3 <i>m/z</i> 253.2/232.9 (quantification)</p> <p>Fluroxypyr Q1/Q3 <i>m/z</i> 253.2/195.0 (confirmation)</p>
Linearity	<p>For the linear regression analysis describing the detector response as a function of the standard calibration curve concentrations, the coefficients of determination (r^2) were all equal to or greater than 0.99 for all of the quantitative calibration curve determinations during the method validation study. The results indicate linearity of the detector response as a function of the standard concentration.</p>
Accuracy	<p>The average recoveries for fluroxypyr in all of the agricultural commodities were between 70 and 110% with the exception of oily crops. While the overall and individual recoveries of fluroxypyr in oily crops were not between the required range (70-110%) according to the current guidelines, SANCO/825/00, they were very consistent with the results obtained in the original method validation (IIIA1 5.3.1/05) with low relative standard deviations and therefore considered acceptable.</p>
Repeatability	<p>The relative standard deviations (RSDs) obtained at each fortification level obtained were in the range 0.89% to 6.7%. Results obtained were within guideline requirements (RSD \leq 20%).</p>

Validation Data					
Matrices	Fortification Level (mg/kg)	Recovery Rate (%)		% RSD	n
		Mean	Range		
Quantification Transition Q1/Q3 m/z 253.2/232.9					
Acidic crops (apples)	0.01	94	91-95	1.7	5
	0.10	98	96-99	0.89	5
	Overall	96	91-99	2.3	10
Dry crops (Hay)	0.01	99	94-105	5.1	5
	0.10	90	85-94	4.1	5
	Overall	95	85-105	6.9	10
Oily crops (Olives)	0.01	71	70-74	2.6	5
	0.10	60	54-63	6.7	5
	Overall	65	54-74	9.9	10
Wet crops (Grass)	0.01	97	93-101	3.2	5
	0.10	92	88-95	3.4	5
	Overall	94	88-101	4.1	10
Bovine Milk	0.01	96	90-102	5.2	5
	0.10	90	86-94	3.5	5
	Overall	93	86-102	5.3	10
Confirmatory Transition Q1/Q3 m/z 253.2/195					
Acidic crops (apples)	0.01	95	91-99	4.0	5
	0.10	97	95-100	1.8	5
	Overall	96	91-100	3.2	10
Dry crops (Hay)	0.01	93	88-98	4.5	5
	0.10	99	98-100	0.84	5
	Overall	96	88-100	4.6	10
Oily crops (Olives)	0.01	72	69-75	3.1	5
	0.10	61	57-63	4.8	5
	Overall	67	57-75	9.7	10
Wet crops (Grass)	0.01	100	99-101	1.2	5
	0.10	94	90-97	3.4	5
	Overall	97	90-101	4.3	10
Bovine Milk	0.01	98	93-103	4.3	5
	0.10	93	89-96	2.7	5
	Overall	95	89-103	4.3	10

Animal Matrices

Clopyralid

Methods for the determination of clopyralid residues in plants, plant products, processed food commodities and animal products have been described in **Volume 3- B.5 (AS)**, Point 4.2 (a) and the animal tissue methods are summarised in **Table 5.2(a)-04**. Picloram is included in the method validation summary since both picloram and clopyralid were validated in the same method due to their similarity in structure.

Table 5.2(a)-04: EU Conclusions: Analytical methods for residues of clopyralid in animal products

Crop/Matrix	EU Agreed Method ¹			Proposed Method ²			
	Method	Analyte	LOQ (mg/kg)	Method	Analyte	LOQ (mg/kg)	Reference
Animal Tissue Matrices	GC/MSD	Clopyralid	0.01				
Animal Tissue Matrices				LC-MS/MS	Clopyralid	0.01	DAS 120483, 2012 (Validation)
Animal Tissue Matrices				LC-MS/MS	Clopyralid	0.01	DAS 120484, 2012 (ILV)

¹ EFSA Scientific Report (2005) 50, 1-65.

² New methods that comply with SANCO 825/00 rev 8.1 have been submitted as part of the Annex I renewal of clopyralid.

Florasulam

Analytical methods are active substance data and were provided in the EU review of florasulam and **were considered adequate**. The current methods available for the determination of residues of florasulam in animal matrices are summarised in **Table 5.2(a)-05**.

Table 5.2(a)-05: EU Conclusions: Analytical methods for residues of florasulam in animal matrices

Crop/Matrix	EU Agreed Method ¹			Proposed Method ²			
	Method	Analyte	LOQ (mg/kg)	Method	Analyte	LOQ (mg/kg)	Reference
Animal Tissue Matrices	LC-MS/MS	Florasulam	0.01	-	-	-	-

¹ Report EFSA Journal 2015;13(1):3984

² Since active substance renewal, no new methods have been developed.

Fluroxypyr (fluroxypyr-meptyl)

All analytical methods are active substance data and were provided in the EU review of fluroxypyr (fluroxypyr-meptyl) and **were considered adequate**. Details of the EU agreed methods for determination of fluroxypyr-meptyl residues in animal products are provided below in **Table 5.2(a)-06**. Since Annex I inclusion, **no new methods have been developed**.

Table 5.2(a)-06: EU Conclusions: Analytical methods for residues of fluroxypyr in animal products

Crop/Matrix	EU Agreed Method ¹				Proposed method ²		
	Method	Analyte	LOQ (mg/kg)	Reference	Method	Analyte	LOQ (mg/kg)
Animal Tissue Matrices	GC-MS/MS	Fluroxypyr and its salts	0.01	-	-	-	-
Animal Tissue Matrices	LC-MS/MS	Fluroxypyr and its salts	0.01	██████████, 2009 (Validation)	-	-	-
Animal Tissue Matrices	LC-MS/MS	Fluroxypyr and its salts	0.01	██████████ 2009 (ILV)			

¹ Review Report EFSA Journal 2011; 9(3); 2091

² Since Annex I inclusion, no new methods have been developed.

B.5.2.2 Methods for the determination of residues in body fluids and tissues

Clopyralid

A method for the determination of clopyralid in body fluids has been described in **Volume 3- B.5 (AS)**, Point 4.2 (d) and is summarised in **Table 5.2(b)-01**.

Table 5.2(b)-01: EU Conclusions: Analytical methods for residues of clopyralid in body fluids

Matrix	EU agreed method ¹			Proposed method ²			
	Method	Analyte	LOQ (mg/L)	Method	Analyte	LOQ (mg/L)	Reference
Body Fluids				LC-MS/MS	Clopyralid	0.05	DAS 130727, 2014

² New methods that comply with SANCO 825/00 rev 8.1 have been submitted as part of the Annex I renewal of clopyralid.

Florasulam

All analytical methods are active substance data and were provided in the EU review of florasulam and were considered adequate. Details of the EU agreed methods are given below in **Table 5.8-01**.

Table 5.2(b)-02: EU Conclusions: Analytical methods for residues of florasulam in body fluids

Matrix	EU agreed method ¹			Proposed method ²			
	Method	Analyte	LOQ (mg/L)	Method	Analyte	LOQ (mg/L)	Reference
Body Fluids	LC-MS/MS	Florasulam	0.05 mg/L	-	-	-	-

¹ Report EFSA Journal 2015;13(1):3984

² Since active substance renewal, no new methods have been developed.

Fluroxypyr (fluroxypyr-meptyl)

No information given.

B.5.2.3 Methods for the determination of residues in soil

Clopyralid

Methods for the determination of residues of clopyralid in soil have been described **Volume 3- B.5 (AS)**, Point 4.2 (b) and are summarised in **Table 5.2(c)-01**. Picloram is included in the method validation summary since both picloram and clopyralid were validated in the same method due to their similarity in structure.

Table 5.2(c)-01 EU Conclusions: Analytical methods for residues of clopyralid in soil

Matrix	EU agreed method ¹			Proposed method ²			
	Method	Analyte	LOQ (µg/kg)	Method	Analyte	LOQ (µg/kg)	Reference
Soil	GC/MSD	Clopyralid	0.5	-	-	-	-
				LC-MS/MS	Clopyralid and Picloram	0.5	DAS 120612, Vincent, T. P., 2013 (Validation)
				LC-MS/MS	Clopyralid and Picloram	0.5	DAS 140079, Austin, R., Turner, R., 2014 (ILV)

¹ EFSA Scientific Report (2005) 50, 1-65.

² New methods that comply with SANCO 825/00 rev 8.1 have been submitted as part of the Annex I renewal of clopyralid.

Florasulam

All analytical methods are active substance data and were provided in the EU review of florasulam and **were considered adequate**. Details of the EU agreed methods are provided below in **Table 5.2(c)-02**.

Table 5.2(c)-02 EU Conclusions: Analytical methods for residues of florasulam in soil

Matrix	EU Agreed Method ¹			Proposed Method ²			
	Method	Analyte	LOQ (µg/kg)	Method	Analyte	LOQ (mg/kg)	Reference
Soil	LC-MS/MS	Florasulam and its metabolite 5-OH	0.05	-	-	-	-

¹ Report EFSA Journal 2015;13(1):3984

² Since active substance renewal, no new methods have been developed.

Fluroxypyr (fluroxypyr-meptyl)

All analytical methods are active substance data and were provided in the EU review of fluroxypyr and **were considered adequate**. Details of the EU agreed methods are provided below in **Table 5.2(c)-03**. Since Annex I inclusion, **new methods have been developed** to incorporate the use of LC-MS/MS and a full summary of the method validation is provided below. However, **they have not been accessed in this context**.

Table 5.2(c)-03 EU Conclusions: Analytical methods for residues of fluroxypyr, fluroxypyr-meptyl in soil

Matrix	EU agreed method ¹			Proposed method ²			
	Method	Analyte	LOQ (mg/kg)	Method	Analyte	LOQ (mg/kg)	Reference
Soil	GC-MS	Fluroxypyr	0.01	-	-	-	-
	-	-	-	LC-MS/MS	Fluroxypyr, Fluroxypyr 1-MHE and metabolites	0.01	DAS 081041, Shackelford, D., 2009

¹ Review Report EFSA Journal 2011; 9(3); 2091

² Since Annex I inclusion, new methods have been developed and a full study summary is provided below.

The following residue analytical study in soil has not been previously reviewed and are provided in support of this assessment. However, **as it is active substance data, it has not been accessed in this context.**

Method Validation for the Determination of Fluroxypyr 1-Methylheptyl Ester and Fluroxypyr and its Major Metabolites in Soil

Report:	Shackelford, D., 2009
Title:	Validation Report for Method GRM 08.06 - Determination of Residues of Fluroxypyr 1-Methylheptyl Ester and Fluroxypyr and its Major Metabolites in Soil by Liquid Chromatography with Tandem Mass Spectrometry
Document No:	Method Report Number 081041
Guidelines:	US EPA OPPTS 850.7100 SANCO/3029/99 rev. 4 and SANCO/825/00 rev. 7 Dir98-02
GLP	Yes
Matrix, limit of determination	0.01 µg/g (mg/kg) for all analytes

Description	<p>Residues of fluroxypyr 1-MHE and fluroxypyr, along with its major metabolites, fluroxypyr-DCP and fluroxypyr-MP are extracted twice from soil with an acetone/0.1 N hydrochloric acid (90:10) solution.</p> <p>First, an aliquot is taken for the determination of fluroxypyr, fluroxypyr-DCP and fluroxypyr-MP. The acetone is removed from the sample aliquot by evaporation. The sample is diluted with a 0.1N hydrochloric acid solution and purified using a Strata-X polymeric solid phase extraction (SPE) cartridge. The SPE cartridge is conditioned with acetonitrile followed by 0.5N hydrochloric acid. Then the SPE cartridge is washed with an acetonitrile/0.1N hydrochloric acid (20:80) solution and dried under vacuum. The analytes are eluted with an acetonitrile/0.1N hydrochloric acid (70:30) solution, and the residues are diluted in a methanol/water (50:50) solution containing 0.1% acetic acid for analysis.</p> <p>Another aliquot is taken for the determination of fluroxypyr 1-MHE. The acetone is removed from the sample aliquot by evaporation, and the residues are reconstituted in a methanol/water (50:50) solution containing 0.1% acetic acid for analysis without any further clean-up or concentration steps.</p> <p>The samples are analysed by liquid chromatography (LC) with positive ion electrospray ionization (ESI) tandem mass spectrometry (MS/MS) for fluroxypyr-DCP and fluroxypyr-MP, and by LC with negative ion ESI with MS/MS for fluroxypyr 1-MHE and fluroxypyr.</p>
Specificity	<p>The method is highly selective for the determination of fluroxypyr analytes by virtue of the chromatographic separation and selective detection system used. To further confirm the presence of fluroxypyr 1-MHE, one additional MS/MS ion transition was monitored at Q1/Q3 m/z 365.1/158.2; for fluroxypyr, one additional MS/MS ion transition was monitored at Q1/Q3 m/z 252.9/194.9; for fluroxypyr-DCP, one additional MS/MS ion transition was monitored at Q1/Q3 m/z 196.9/152.2; and to further confirm the presence of fluroxypyr-MP, one additional MS/MS ion transition was monitored at Q1/Q3 m/z 210.9/113.0.</p>
Linearity	<p>For the linear regression analysis, the coefficients of determination (r^2) were all equal to or greater than 0.9988 for all of the calibration curve determinations during the method validation. The results indicate linearity of the detector response as a function of the standard concentration.</p>
Accuracy	<p>The average recoveries at each fortification level for fluroxypyr, fluroxypyr 1-MHE and its metabolites in soil were between 70% and 97% which are within the guideline requirement, SANCO/825/00 rev 8.1 (70-110%).</p>

Repeatability	Repeatability at each fortification level, as demonstrated by the relative standard deviation RSD, was always ≤ 6.6 % which is within the guideline requirements (RSD≤20%).				
Validation Data in Soil					
Analytes	Fortification Level (mg/kg)	Recovery Rates (%)		% RSD	n
		Mean	Range		
Quantification Transition					
Fluroxypyr 1-MHE	0.01	87	83-91	3.1	12
	0.10	90	89-92	1.7	6
	1.00	94	89-101	3.5	9
	Overall	90	83-101	4.6	27
Fluroxypyr	0.01	95	83-104	6.6	12
	0.10	97	90-106	5.8	6
	1.00	94	90-97	2.8	9
	Overall	95	83-106	5.4	27
Fluroxypyr-DCP	0.01	92	84-97	4.8	12
	0.10	91	85-96	4.0	6
	1.00	93	88-97	3.0	9
	Overall	92	84-97	4.1	27
Fluroxypyr-MP	0.01	81	73-89	5.3	12
	0.10	70	67-74	3.7	6
	1.00	71	66-75	4.4	9
	Overall	75	66-89	8.4	27

B.5.2.4 Methods for the determination of residues in water

Clopyralid

Methods for the determination of residues of clopyralid in water have been described in **Volume 3- B.5 (AS)**, Point 4.2 (b) and are summarised in **Table 5.2(d)-01**. Picloram is included in the method validation summary since both picloram and clopyralid were validated in the same method due to their similarity in structure.

Table 5.2(d)-01 EU Conclusions: Analytical methods for residues of clopyralid in water

Matrix	EU agreed method ¹			Proposed method ²			
	Method	Analyte	LOQ (µg/L)	Method	Analyte	LOQ (µg/L)	Reference
Surface, ground and drinking water	GC/MSD	Clopyralid	0.050	-	-	-	-
				LC-MS/MS	Clopyralid and Picloram	0.050	DAS 120611, Shaffer, S., 2012 (Validation)
				LC-MS/MS	Clopyralid and Picloram	0.050	DAS 120613, Austin, R., Turner, R., 2013 (ILV)

¹ EFSA Scientific Report (2005) 50, 1-65.

² New methods that comply with SANCO 825/00 rev 8.1 have been submitted as part of the Annex I renewal of clopyralid.

Florasulam

All analytical methods are active substance data and were provided in the EU review of florasulam and **were considered adequate**. Details of the EU agreed methods are provided below in **Table 5.2(d)-02**.

Table 5.2(d)-02: EU Conclusions: Analytical methods for residues of florasulam in water

Matrix	EU agreed method ¹			Proposed method ²			
	Method	Analyte	LOQ (µg/L)	Method	Analyte	LOQ (µg/L)	Reference
Water	LC-MS/MS	Florasulam and its 5-OH metabolite	0.05	-	-	-	-

¹ Report EFSA Journal 2015;13(1):3984

² Since active substance renewal, no new methods have been developed.

Fluroxypyr 1-MHE, fluroxypyr and its metabolites

All analytical methods are active substance data and were provided in the EU review of fluroxypyr (fluroxypyr-meptyl) active substance and **were considered adequate**. Details of the EU agreed methods are provided below in **Table 5.2(d)-03**. Since Annex I inclusion, **new methods have been developed** to incorporate the use of LC-MS/MS and a full summary of the method validation is provided below. However, **they have not been accessed in this context**.

Table 5.2(d)-03: EU Conclusions: Analytical methods for residues of fluroxypyr, fluroxypyr-meptyl in water

Analyte	EU agreed method ¹			Proposed method ²			
	Method	Analyte	LOQ (µg/L)	Method	Analyte	LOQ (µg/L)	Reference
Surface water	GC-MS	fluroxypyr-MHE, fluroxypyr and its salts, fluroxypyr-2-pyridinol, and fluroxypyr-2-methoxypyridine	5.0	-	-	-	-
Drinking water Ground water Surface water	-	-	-	LC-MS/MS	Fluroxypyr 1MHE, Fluroxypyr and its Major Metabolites	0.05	DAS 081042, Shackelford, D., 2010 (Validation)
	-	-	-	LC-MS/MS	Fluroxypyr 1MHE, Fluroxypyr and its Major Metabolites	0.05	DAS 101083, Austin, R., 2010 (ILV)

¹ Review Report EFSA Journal 2011; 9(3); 2091

² Since Annex I inclusion, new methods have been developed and a full summary is provided below.

The following residue analytical studies on water have not been previously reviewed and are provided in support of this assessment. However, **as they are active substance data, they have not been accessed in this context.**

Method Validation for the Determination of Fluroxypyr 1 Methylheptyl Ester, Fluroxypyr and its Major Metabolites in Water

Report:	Shackelford, D. (2010)										
Title:	Validation Report for the Determination of Residues of Fluroxypyr 1 Methylheptyl Ester, Fluroxypyr and its Major Metabolites in Surface Water, Ground Water and Drinking Water by High Performance Liquid Chromatography with Tandem Mass Spectrometry *AMENDED REPORT*										
Document No:	Method Report Number 081042										
Guidelines:	OPPTS 850.7100 SANCO/3029/00 rev.4 SANCO/825/00 rev 7 Dir98-02										
GLP	Yes										
Matrix, limit of determination	0.05 µg/L for each analyte										
Description	<p>Residues of fluroxypyr 1-MHE and fluroxypyr are extracted from the water sample matrices by acidifying the sample using concentrated formic acid, saturating the water with sodium chloride, then partitioning it twice against ethyl acetate. The two ethyl acetate layers are drawn off and combined in the same graduated Nalgene tube. A 1.0 mL aliquot of a methanol/water (50:50) solution containing 0.1% acetic acid solution is added. The combined ethyl acetate extracts are concentrated under a stream of nitrogen until approximately 0.7-0.9 mL remains. The final sample is adjusted to 2.0 mL using a methanol/water (50:50) solution containing 0.1% acetic acid. The sample is analysed by liquid chromatography with negative-ion electrospray ionization (ESI) tandem mass spectrometry (LC/MS/MS).</p> <p>For the determination of residues of fluroxypyr-DCP and fluroxypyr-MP, the water samples are buffered to pH 7 using a potassium dihydrogen phosphate buffer solution. The water sample is loaded onto a Strata -X polymeric sorbent SPE column and eluted with acetonitrile into a graduated Nalgene tube containing a 1.0-mL aliquot of a methanol/water (50:50) solution with 0.1% acetic acid solution added. The acetonitrile eluate is concentrated under a stream of nitrogen until approximately 0.7-0.9 mL remains. The final sample is adjusted to 1.5 mL using a methanol/water (50:50) solution containing 0.1% acetic acid. The sample is analysed by liquid chromatography with positive-ion atmospheric pressure chemical ionization (APCI) tandem mass spectrometry (LC/MS/MS).</p>										
Specificity	<p>The method is selective for the determination of fluroxypyr 1-MHE and fluroxypyr, along with its major metabolites, fluroxypyr-DCP and fluroxypyr-MP in surface water, ground water and drinking water by virtue of the chromatographic separation and selective detection system used. To demonstrate further confirmation, additional fluroxypyr 1-MHE and fluroxypyr, fluroxypyr-DCP and fluroxypyr-MP ion transitions can be monitored as follows:</p> <table> <tr> <td>Fluroxypyr 1-MHE</td><td>Q1/Q3 m/z 365.1/194.1 (quantification)</td></tr> <tr> <td>Fluroxypyr 1-MHE</td><td>Q1/Q3 m/z 367.0/196.0 (confirmation)</td></tr> <tr> <td>Fluroxypyr</td><td>Q1/Q3 m/z 252.9/232.9 (quantification)</td></tr> <tr> <td>Fluroxypyr</td><td>Q1/Q3 m/z 255.0/196.8 (confirmation)</td></tr> <tr> <td>Fluroxypyr-DCP</td><td>Q1/Q3 m/z 199.0/181.0 (quantification)</td></tr> </table>	Fluroxypyr 1-MHE	Q1/Q3 m/z 365.1/194.1 (quantification)	Fluroxypyr 1-MHE	Q1/Q3 m/z 367.0/196.0 (confirmation)	Fluroxypyr	Q1/Q3 m/z 252.9/232.9 (quantification)	Fluroxypyr	Q1/Q3 m/z 255.0/196.8 (confirmation)	Fluroxypyr-DCP	Q1/Q3 m/z 199.0/181.0 (quantification)
Fluroxypyr 1-MHE	Q1/Q3 m/z 365.1/194.1 (quantification)										
Fluroxypyr 1-MHE	Q1/Q3 m/z 367.0/196.0 (confirmation)										
Fluroxypyr	Q1/Q3 m/z 252.9/232.9 (quantification)										
Fluroxypyr	Q1/Q3 m/z 255.0/196.8 (confirmation)										
Fluroxypyr-DCP	Q1/Q3 m/z 199.0/181.0 (quantification)										

	Fluroxypyr-DCP	Q1/Q3 m/z 199.0/154.1 (confirmation)			
	Fluroxypyr-MP	Q1/Q3 m/z 210.9/113.2 (quantification)			
	Fluroxypyr-MP	Q1/Q3 m/z 210.9/196.1 (confirmation)			
Linearity	For the linear regression analysis describing the detector response as a function of the standard calibration curve concentrations, the coefficients of determination (r^2) were all equal to or greater than 0.9981 for all of the quantitative calibration curve determinations for each of the analytes during the method validation study. The results indicate linearity of the detector response as a function of the standard concentration.				
Accuracy	The overall average recoveries for fluroxypyr, fluroxypyr 1-MHE, fluroxypyr-DCP and fluroxypyr-MP in drinking, ground and surface water were between 71% and 103% which are within the guideline requirement, SANCO/825/00 rev 8.1 (70-110%) with the exception of surface water at 0.05 ng/mL which had an average recovery for fluroxypyr 1-MHE of 66%. While the recoveries for fluroxypyr 1-MHE at 0.05 ng/mL were sometimes lower than 70%, they were typically very consistent and the standard deviations were low. In addition, acceptable recovery was obtained in the ILV for fluroxypyr 1-MHE in surface water and is reported below.				
Repeatability	Repeatability, as demonstrated by the relative standard deviation RSD, was always ≤ 20 % except for the recovery of fluroxypyr 1-MHE from surface water at 0.5 mg/kg. However, acceptable repeatability was obtained during the ILV performed below which shows that the method is acceptable.				
Validation Data					
Analytes	Fortification Level ($\mu\text{g/L}$)	Recovery Rate (%)		% Relative Standard Deviation	n
		Mean	Range		
Drinking Water					
Fluroxypyr 1-MHE	0.05	63	55-78	14.5	5
	0.50	74	72-77	3.0	3
	5.00	76	71-81	5.7	5
	Overall	71	55-81	12.1	13
Fluroxypyr	0.05	94	88-102	6.6	5
	0.50	90	88-92	2.5	3
	5.00	94	90-97	2.5	5
	Overall	93	88-102	4.7	13
Fluroxypyr-DCP	0.05	101	87-115	12.1	5
	0.50	99	98-100	1.2	3
	5.00	97	94-104	4.6	5
	Overall	99	87-115	7.9	13
Fluroxypyr-MP	0.05	104	95-123	10.9	5
	0.50	99	94-103	4.9	3
	5.00	89	84-92	3.4	5
	Overall	97	84-123	10.1	13
Ground Water					
Fluroxypyr 1-MHE	0.05	74	60-86	12.5	5
	0.50	79	71-88	10.7	3
	5.00	83	80-87	4.3	5

	Overall	79	60-88	10.2	13
Fluroxypyr	0.05	99	93-109	6.5	5
	0.50	95	90-101	5.4	3
	5.00	96	91-102	5.1	5
	Overall	97	90-109	5.6	13
Fluroxypyr-DCP	0.05	103	92-112	7.8	5
	0.50	98	96-100	2.3	3
	5.00	99	97-102	2.2	5
	Overall	100	92-112	5.3	13
Fluroxypyr-MP	0.05	91	75-107	15.8	5
	0.50	96	92-101	4.8	3
	5.00	94	91-96	2.1	5
	Overall	93	75-107	9.5	13
Surface Water					
Fluroxypyr 1-MHE	0.05	66	61-73	7.1	5
	0.50	52	41-65	23.2	3
	5.00	74	62-81	9.8	5
	Overall	66	41-81	16.8	13
Fluroxypyr	0.05	111	96-122	9.9	5
	0.50	107	97-114	8.1	3
	5.00	92	88-97	4.0	5
	Overall	103	88-122	11.4	13
Fluroxypyr-DCP	0.05	100	92-114	8.2	5
	0.50	95	89-101	6.4	3
	5.00	96	92-101	4.0	5
	Overall	98	89-114	6.5	13
Fluroxypyr-MP	0.05	102	85-112	10.5	5
	0.50	93	88-99	6.0	3
	5.00	92	82-100	7.7	5
	Overall	96	82-112	9.5	13

Independent Laboratory Validation of the Method for the Determination of Fluroxypyr 1-Methylheptyl Ester, Fluroxypyr and its Major Metabolites in Water

Report:	Austin, R. (2010b)
Title:	Independent Laboratory Validation of a Method for the Determination of Residues of Fluroxypyr 1-Methylheptyl Ester, Fluroxypyr and its Major Metabolites in Surface Water, Ground Water and Drinking Water
Document No:	CEMAS Study No : CEMS-4626; DAS Report Number 101083
Guidelines:	OECD Principles of Good Laboratory Practice UK Good Laboratory Practice Regulations 1999 (S.I. 1999/3106, as amended by S.I. 994, 2004) OPPTS 850.7100 SANCO/3029/99 rev.4 SANCO/825/00 rev.7
GLP	Yes
Matrix, limit of determination	0.05 µg/L for each analyte
Description	<p>Residues of fluroxypyr 1-MHE and fluroxypyr are extracted from the water sample matrices by acidifying the sample using concentrated formic acid, saturating the water with sodium chloride, then partitioning it twice against ethyl acetate. The two ethyl acetate layers are drawn off and combined in the same graduated Nalgene tube. A 1.0 mL aliquot of a methanol/water (50:50) solution containing 0.1% acetic acid solution is added. The combined ethyl acetate extracts are concentrated under a stream of nitrogen until approximately 0.7-0.9 mL remains. The final sample is adjusted to 2.0 mL using a methanol/water (50:50) solution containing 0.1% acetic acid. The sample is analysed by liquid chromatography with negative-ion electrospray ionization (ESI) tandem mass spectrometry (LC/MS/MS).</p> <p>For the determination of residues of fluroxypyr-DCP and fluroxypyr-MP, the water samples are buffered to pH 7 using a potassium dihydrogen phosphate buffer solution. The water sample is loaded onto a Strata -X polymeric sorbent SPE column and eluted with acetonitrile into a graduated Nalgene tube containing a 1.0-mL aliquot of a methanol/water (50:50) solution with 0.1% acetic acid solution is added. The acetonitrile eluate is concentrated under a stream of nitrogen until approximately 0.7-0.9 mL remains. The final sample is adjusted to 1.5 mL using a methanol/water (50:50) solution containing 0.1% acetic acid. The sample is analysed by liquid chromatography with positive-ion atmospheric pressure chemical ionization (APCI) tandem mass spectrometry (LC/MS/MS).</p>
Specificity	The method is selective for the determination of fluroxypyr 1-MHE and fluroxypyr, along with its major metabolites, fluroxypyr-DCP and fluroxypyr-MP in surface water, ground water and drinking water by virtue of the chromatographic separation and selective detection system used. To demonstrate further confirmation, additional fluroxypyr

	1-MHE and fluroxypyr, fluroxypyr-DCP and fluroxypyr-MP ion transitions can be monitored as follows:				
	Fluroxypyr 1-MHE		Q1/Q3 <i>m/z</i> 365.2/194.1 (quantification)		
	Fluroxypyr 1-MHE		Q1/Q3 <i>m/z</i> 367.2/196.3 (confirmation)		
	Fluroxypyr		Q1/Q3 <i>m/z</i> 253.2/232.9 (quantification)		
	Fluroxypyr		Q1/Q3 <i>m/z</i> 255.1/197.0 (confirmation)		
	Fluroxypyr-DCP		Q1/Q3 <i>m/z</i> 199.14/181.0 (quantification)		
	Fluroxypyr-DCP		Q1/Q3 <i>m/z</i> 199.14/154.0 (confirmation)		
	Fluroxypyr-MP		Q1/Q3 <i>m/z</i> 211.17/113.0 (quantification)		
	Fluroxypyr-MP		Q1/Q3 <i>m/z</i> 211.17/195.9 (confirmation)		
Accuracy	The overall average recoveries for fluroxypyr, fluroxypyr 1-MHE, fluroxypyr-DCP and fluroxypyr-MP in drinking, ground and surface water were between 84% and 95% which are within the guideline requirement, SANCO/825/00 rev 8.1 (70-110%).				
Repeatability	Repeatability, as demonstrated by the relative standard deviation RSD, was always ≤ 20 %.				
Linearity	For the linear regression analysis describing the detector response as a function of the standard calibration curve concentrations, the coefficients of determination (r ²) were all equal to or greater than 0.9981 for all of the quantitative calibration curve determinations for each of the analytes during the method validation study. The results indicate linearity of the detector response as a function of the standard concentration.				
Validation Data					
Analytes	Fortification Level (µg/L)	Recovery Rate (%)		% Relative Standard Deviation	n
		Mean	Range		
Quantification Transition					
Drinking Water					
fluroxypyr 1-MHE	0.05	93	92-96	2.1	5
	0.50	94	89-100	5.9	5
	Overall	93	89-100	4.2	10
fluroxypyr	0.05	89	83-93	4.3	5
	0.50	87	83-89	2.8	5
	Overall	88	83-93	3.8	10
fluroxypyr-DCP	0.05	99	94-106	5.6	5
	0.50	84	79-89	4.9	5
	Overall	91	79-106	10.2	10
fluroxypyr-MP	0.05	90	79-103	10.2	5
	0.50	80	75-89	6.9	5

	Overall	85	75-103	10.5	10
Ground Water					
fluroxypyr 1-MHE	0.05	92	81-96	7	5
	0.50	94	89-99	5	5
	Overall	93	81-99	5.9	10
fluroxypyr	0.05	86	80-97	7.5	5
	0.50	87	83-92	4.6	5
	Overall	87	80-97	5.9	10
fluroxypyr-DCP	0.05	90	86-99	5.7	5
	0.50	92	88-96	3.3	5
	Overall	91	86-99	4.5	10
fluroxypyr-MP	0.05	83	80-86	2.7	5
	0.50	85	79-90	5	5
	Overall	84	79-90	3.9	10
Surface Water					
fluroxypyr 1-MHE	0.05	93	87-98	5	5
	0.50	98	92-101	3.7	5
	Overall	95	87-101	5	10
fluroxypyr	0.05	85	80-90	4.4	5
	0.50	83	80-88	3.5	5
	Overall	84	80-90	3.9	10
fluroxypyr-DCP	0.05	86	62-100	17.4	5
	0.50	89	67-97	14.2	5
	Overall	88	62-100	15	10
fluroxypyr-MP	0.05	86	84-87	1.6	5
	0.50	89	82-95	5.4	5
	Overall	87	82-95	4.4	10
Confirmatory Transition					
Drinking Water					
fluroxypyr 1-MHE	0.05	97	94-99	2.1	5
	0.50	98	93-103	4.6	5
	Overall	97	93-103	3.4	10
fluroxypyr	0.05	89	86-96	4.6	5
	0.50	88	85-90	2.6	5
	Overall	88	85-96	3.7	10
fluroxypyr-DCP	0.05	101	92-111	8.8	5
	0.50	89	80-101	8.5	5

	Overall	95	80-111	10.6	10
fluroxypyr-MP	0.05	90	83-107	10.8	5
	0.50	79	73-86	6.2	5
	Overall	84	73-107	11.1	10
Ground Water					
fluroxypyr 1-MHE	0.05	94	84-100	6.9	5
	0.50	91	86-96	4.4	5
	Overall	93	84-100	5.7	10
fluroxypyr	0.05	83	80-88	4.2	5
	0.50	84	80-90	5.1	5
	Overall	83	80-90	4.4	10
fluroxypyr-DCP	0.05	94	92-97	2.5	5
	0.50	92	85-96	4.5	5
	Overall	93	85-97	3.6	10
fluroxypyr-MP	0.05	84	81-87	2.5	5
	0.50	84	77-88	5.0	5
	Overall	84	77-88	3.8	10
Surface Water					
fluroxypyr 1-MHE	0.05	95	87-102	6.2	5
	0.50	96	92-103	4.8	5
	Overall	96	87-103	5.3	10
fluroxypyr	0.05	94	90-99	4.4	5
	0.50	83	78-87	7.6	5
	Overall	88	78-99	7.6	10
fluroxypyr-DCP	0.05	88	61-100	17.6	5
	0.50	88	66-98	14.6	5
	Overall	88	61-100	15.2	10
fluroxypyr-MP	0.05	79	76-83	3.1	5
	0.50	89	84-92	4.0	5
	Overall	84	76-92	7.0	10

B.5.2.5 Methods for the determination of residues in air, unless the applicant shows that exposure of operators, workers, residents or bystanders is negligible

Clopyralid

Methods for the determination of residues of clopyralid in air have been described in **Volume 3- B.5 (AS)**, Point 4.2 (c) and additional methods for the formulation are not required. Details of the methods are given below in **Table 5.2(e)-01**.

Table 5.2(e)-01 EU Conclusions: Analytical methods for residues of clopyralid in air

Matrix	EU agreed method ¹			Proposed method ²			
	Method	Analyte	LOQ (µg/m ³)	Method	Analyte	LOQ (µg/m ³)	Reference
Air	GC/MSD	Clopyralid	15	-	-	-	-

¹ EFSA Scientific Report (2005) 50, 1-65.

² Since Annex I inclusion, no new methods have been developed.

Florasulam

All analytical methods are active substance data and were provided in the EU review of florasulam and **were considered adequate**. Details of the EU agreed methods are given below in **Table 5.2(e)-02**.

Table 5.2(e)-02: EU Conclusions: Analytical methods for residues of florasulam in air

Matrix	EU agreed method ¹			Proposed method ²			
	Method	Analyte	LOQ (µg/m ³)	Method	Analyte	LOQ (µg/m ³)	Reference
Air	LC-MS/MS	Florasulam	1.5	-	-	-	-

¹ Report EFSA Journal 2015;13(1):3984

² Since active substance renewal, no new methods have been developed.

Fluroxypyr

All analytical methods are active substance data and were provided in the EU review of fluroxypyr active substance. No further methods have been developed since Annex I inclusion. Details of the EU agreed methods are given below in **Table 5.2(e)-03**.

Table 5.2(e)-03 EU Conclusions: Analytical methods for residues of fluroxypyr in air

Analyte	EU agreed method ¹			Proposed method ²			
	Method number	Analyte	LOQ (µg/m ³)	Method number	Analyte	LOQ (mg/kg)	Reference
Air	LC-MS/MS	Fluroxypyr	24	-	-	-	-

¹ Review Report EFSA Journal 2011; 9(3); 2091

² Since Annex I inclusion, no further methods have been developed.

B.5.3. REFERENCES RELIED ON

GF-1374 was not the representative formulation for the Active Approval of active clopyralid.

Data owner: DAS = Dow AgroSciences

Data Point	Author(s)	Year	Title Source (where different from company) Company Report No. Date GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
CP 5.1.1/1	Cathie, C.A.	2005	Validation of a Method for the Determination of Clopyralid, Florasulam and Fluroxypyr meptyl in GF-1374 Dow AgroSciences LTD, New Plymouth, New Zealand DAS-AM-05-004 1.11.2005 GLP/GEP (Y/N): Y Published (Y/N): N	No	Yes	H**)	DAS	Submitted for the purpose of renewal
CP 5.1.2 (f)/1 (submitted under CP 10.6.2/1)	Eley, R.	2005a; amended 2008	Evaluation of the Phytotoxicity of GF-1374 (Fluroxypyr-1-MHE +Clopyralid+Florasulam, EC) GLP Vegetative Vigour Test - Terrestrial Non Target Plants (Based on OECD Guideline 208 B) North Europe 2005. AgroChemex Ltd., Aldhams Farm, Manningtree, C011 2NF, UK. Analytical report performed in Huntingdon Life Sciences Ltd., Woolley Road, Alconbury, Huntingdon, Cambridgeshire, PE28 4HS, England Study Number: EA05B2A033 13.12.2005 (analytical report 30.11.2005); amended 27.5.2008 GLP/GEP Yes Published No	No	Yes	H**)	DAS	Submitted for the purpose of renewal

Data Point	Author(s)	Year	Title Source (where different from company) Company Report No. Date GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
CP 5.1.2 (f)/2 (submitted under CP 10.6.2/2)	Eley, R.	2005b; amended 2008	Evaluation of the Phytotoxicity of GF-1374 (Fluroxypr-1-MHE +Clopyralid+Florasulam, 144+80+2.5 g as/l, EC) GLP Seedling Emergence and Seedling Growth Test –Terrestrial Non Target Plants (Based on OECD Guideline 208 A) North Europe 2005. AgroChemex Ltd., Aldhams Farm, Manningtree, C011 2NF, UK. Analytical report performed in Huntingdon Life Sciences Ltd., Woolley Road, Alconbury, Huntingdon, Cambridgeshire, PE28 4HS, England Study Number: EA05B2A020 13.12.2005 (analytical report 30.11.2005); amended 27.5.2008 GLP/GEP Yes Published No	No	Yes	H**)	DAS	Submitted for the purpose of renewal
CP 5.2(a)/1 (See Vol. 3- B.5(AS): CA 4.2 (a)/1)	Vogl, E.	2012	Method Validation Study for the Determination of Residues of Clopyralid and Picloram in Agricultural Commodities by LC-MS/MS ABC Laboratories, Inc., Columbia, Missouri, USA DAS Report No. 120610 GLP/GEP (Y/N): Yes Published (Y/N): No	No	Yes	G*)	DAS	rf. Vol. 3- B.5 (AS)
CP 5.2(a)/2 (See Vol. 3- B.5(AS): CA 4.2 (a)/2)	Austin, R.	2012	Independent Laboratory Validation of Dow AgroSciences Method 120610, “Method Validation Study for the Determination of Residues of Clopyralid and Picloram in Agricultural Commodities by LC-MS/MS” Battelle UK Ltd, Chelmsford, Essex, United Kingdom	No	Yes	G*)	DAS	rf. Vol. 3- B.5 (AS)

Data Point	Author(s)	Year	Title Source (where different from company) Company Report No. Date GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
			DAS Report No. 120614 GLP/GEP (Y/N): Yes Published (Y/N): No					
CP 5.2(a)/3	██████████ ██████	2010	Validation Report for the Determination of Residues of Fluroxypyr 1-methylheptyl Ester as the Acid Equivalent in Agricultural Commodities and Fluroxypyr in Bovine Milk by High Performance Liquid Chromatography with Tandem Mass Spectrometry Dow AgroSciences DAS Report No. 091171 GLP/GEP (Y/N): Yes Published (Y/N): No	No	Yes	G ^{*)}	DAS	Additional information
CP 5.2(a)/4	██████████	2010	Independent Laboratory Validation of a Method for the Determination of Residues of Fluroxypyr 1-methylheptyl Ester as the Acid Equivalent in Agricultural Commodities and Bovine Milk ██████████ DAS Report No. 101082 GLP/GEP (Y/N): Yes Published (Y/N): No	No	Yes	G ^{*)}	DAS	Additional information
CP 5.2(a)/5 (See Vol. 3- B.5(AS): CA 4.2(a)/3)	██████████	2012	Method Validation Study for the Determination of Residues of Clopyralid in Bovine and Poultry Matrices by Liquid Chromatography with Tandem Mass Spectrometry Detection ██ DAS Report No. 120483 GLP/GEP (Y/N): Yes Published (Y/N): No	Yes	Yes	G ^{*)}	DAS	rf. Vol. 3- B.5 (AS)

Data Point	Author(s)	Year	Title Source (where different from company) Company Report No. Date GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
CP 5.2(a)/6 (See Vol. 3- B.5(AS): CA 4.2(a)/4)	████████	2012	Independent Laboratory Validation of an Analytical Method for the Determination of Clopyralid in Animal Matrices ██ DAS Report No. 120484 GLP/GEP (Y/N): Yes Published (Y/N): No	Yes	Yes	G ^{*)}	DAS	rf. Vol. 3- B.5 (AS)
CP 5.2(b)/1 (See Vol. 3- B.5(AS): CA 4.2(d)/1)	████████	2014	Development and Validation of an Analytical Method for the Determination of Clopyralid in Body Fluid(s) ██ DAS Report No. 130727 GLP/GEP (Y/N): Yes Published (Y/N): No	No	Yes	G ^{*)}	DAS	rf. Vol. 3- B.5 (AS)
CP 5.2(c)/1 (See Vol. 3- B.5(AS): CA 4.2(b)/1)	Vincent, T. P.	2013	Method Validation Study for the Determination of Residues of Clopyralid and Picloram in Soil by LCMS/MS ABC Laboratories, Inc., Columbia, Missouri, USA DAS Report No. 120612 GLP/GEP (Y/N): Yes Published (Y/N): No	No	Yes	G ^{*)}	DAS	rf. Vol. 3- B.5 (AS)
CP 5.2(c)/2 (See Vol. 3- B.5(AS): CA 4.2(b)/2)	Austin, R., Turner, R.	2014	Independent Laboratory Validation of a Dow AgroSciences Method for the Determination of Residues of Clopyralid and Picloram in Soil by LC-MS/MS Battelle UK Ltd, Chelmsford, Essex, United Kingdom DAS Report No. 140079 GLP/GEP (Y/N): Yes Published (Y/N): No	No	Yes	G ^{*)}	DAS	rf. Vol. 3- B.5 (AS)

Data Point	Author(s)	Year	Title Source (where different from company) Company Report No. Date GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
CP 5.2(c)/3	Shackelford, D.	2009	Validation Report for Method GRM 08.06 - Determination of Residues of Fluroxypyr 1-Methylheptyl Ester and Fluroxypyr and its Major Metabolites in Soil by Liquid Chromatography with Tandem Mass Spectrometry Dow AgroSciences DAS Report No. 081041 GLP/GEP (Y/N): Yes Published (Y/N): No	No	Yes	G ^{*)}	DAS	Additional information
CP 5.2(d)/1 (See Vol. 3- B.5(AS): CA 4.2(b)/3)	Shaffer, S.	2012	Method Validation Study for the Determination of Residues of Clopyralid and Picloram in Drinking Water, Ground Water, and Surface Water by LCMS/MS ABC Laboratories, Inc., Columbia, Missouri, USA DAS Report No. 120611 GLP/GEP (Y/N): Yes Published (Y/N): No	No	Yes	G ^{*)}	DAS	rf. Vol. 3- B.5 (AS)
CP 5.2(d)/2 (See Vol. 3- B.5(AS): CA 4.2(b)/4)	Austin, R., Turner, R.	2013	Independent Laboratory Validation of Dow AgroSciences Method 120611, "Method Validation Study for the Determination of Residues of Clopyralid and Picloram in Drinking Water, Ground Water, and Surface Water by LC-MS/MS" Battelle UK Ltd, Ongar, Essex, United Kingdom DAS Report No. 120613 GLP/GEP (Y/N): Yes	No	Yes	G ^{*)}	DAS	rf. Vol. 3- B.5 (AS)

Data Point	Author(s)	Year	Title Source (where different from company) Company Report No. Date GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
			Published (Y/N): N					
CP 5.2(d)/3	Shackelford, D.	2010	Validation Report for the Determination of Residues of Fluroxypyr 1 Methylheptyl Ester, Fluroxypyr and its Major Metabolites in Surface Water, Ground Water and Drinking Water by High Performance Liquid Chromatography with Tandem Mass Spectrometry *AMENDED REPORT* Dow AgroSciences DAS Report No. 081042 GLP/GEP (Y/N): Yes Published (Y/N): No	No	Yes	G ^{*)}	DAS	Additional information
CP 5.2(d)/4	Austin, R.	2010	Independent Laboratory Validation of a Method for the Determination of Residues of Fluroxypyr 1-Methylheptyl Ester, Fluroxypyr and its Major Metabolites in Surface Water, Ground Water and Drinking Water CEMAS DAS Report No. 101083 GLP/GEP (Y/N): Yes Published (Y/N): No	No	Yes	G ^{*)}	DAS	Additional information

^{*)}G Product data submitted with an application under Article 47 of the Regulation (low risk products).

^{**)H} Product data submitted with an application for renewal of authorisation under Article 43 of the Regulation – containing at least one active considered under AIR2 onwards.