

**Test Material:** Quizalofop-p-ethyl

**MRID:** 49634805

**Title:** Validation of BASF Analytical Method (D1304/02): "Analytical Method for the Determination of Residues of Quizalofop-p-ethyl (BAS 9152 H) and its two Metabolites Quizalofop-p and 3-OH-Quizalofop-acid in Water by LC-MS/MS"

**MRID:** 49634807

**Title:** Independent Lab Validation of BASF Analytical Method D1304/02: "Analytical Method for the Determination of Residues of Quizalofop-p-ethyl and its Metabolites Quizalofop-p and 3-OH-Quizalofop-acid in Water by LC-MS/MS"

**EPA PC Code:** 128709

**OCSPP Guideline:** 850.6100

**For CDM Smith**

**Primary Reviewer:** Lynne Binari

**Signature:** 

**Date:** 8/18/15

**Secondary Reviewer:** Lisa Muto

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**Date:** 8/18/15

**QC/QA Manager:** Joan Gaidos

**Signature:** 

**Date:** 8/18/15

**Analytical method for quizalofop-p-ethyl (BAS 9152 H) and its transformation products quizalofop-p and 3-OH-quizalofop-acid in water**

**Reports:** ECM: EPA MRID No.: 49634805. Zheng, S. (C.). 2015. Validation of BASF Analytical Method (D1304/02): "Analytical Method for the Determination of Residues of Quizalofop-p-ethyl (BAS 9152 H) and its two Metabolites Quizalofop-p and 3-OH-Quizalofop-acid in Water by LC-MS/MS". Report prepared by Primera Analytical Solutions Corporation (PASC), Princeton, New Jersey, sponsored, and submitted by BASF Corporation, Research Triangle Park, North Carolina; 199 pages. PASC Study No.: 053-0978A and Report No.: PASC-REP-0526. BASF Study No.: 437862 and Registration Document No.: 2014/7003589. Final report issued March 3, 2015.  
ILV: EPA MRID No. 49634807. Sharp, S. 2015. Independent Lab Validation of BASF Analytical Method D1304/02: "Analytical Method for the Determination of Residues of Quizalofop-p-ethyl and its Metabolites Quizalofop-p and 3-OH-Quizalofop-acid in Water by LC-MS/MS". Report prepared by EPL Bio Analytical Services (EPL), Niantic, Illinois, sponsored and submitted by BASF Corporation, Research Triangle Park, North Carolina; 158 pages. EPL Study No.: 137G966. BASF Study No.: 437863 and Registration Document No.: 2014/7003591. Final report issued March 10, 2015.

**Document No.:** MRIDs 49634805 & 49634807

**Guideline:** 850.6100


**Statements:** ECM: The study was conducted in compliance with USEPA Good Laboratory Practice (GLP) standards (40 CFR Part 160; p. 3 of MRID 49634805). Signed and dated Data Confidentiality, GLP, Quality Assurance, and Authenticity Certification statements were provided (pp. 2-5).  
ILV: The study was conducted in compliance with USEPA GLP standards (p. 3 of MRID 49634807). Signed and dated Data Confidentiality, GLP, Quality Assurance, and Authenticity Certification statements were provided (pp. 2-5).

**Classification:** This analytical method is classified as **acceptable**. The determinations of the LOQ and LOD were not based on scientifically acceptable procedures.

**PC Code:** 128709

**Reviewer:**

Stephen P. Wentz  
Biologist

**Signature:**   
**Date:** October 25, 2016

## Executive Summary

The analytical method, BASF Analytical Method D1304/02, is designed for the quantitative determination of quizalofop-p-ethyl (BAS 9152 H) and its transformation products quizalofop-p and 3-OH-quizalofop-acid in water using LC/MS/MS. The method is quantitative for the analytes at the stated LOQ of 0.001 mg/kg (ppm) for all three analytes. The LOQ is less than the lowest toxicological level of concern in water. The independent laboratory validated the method for analysis of quizalofop-p-ethyl at the LOQ and 10x LOQ in drinking (tap) and surface (source not specified) water matrices after one trial and for quizalofop-p and 3-OH-quizalofop-acid at both fortification levels in the two water matrices after two trials. No major modifications were made by the independent laboratory.

**Table 1. Analytical Method Summary**

Analyte(s) by Pesticide	MRID		EPA Review	Matrix	Method Date (dd/mm/yyyy)	Registrant	Analysis	Limit of Quantitation (LOQ)
	Environmental Chemistry Method	Independent Laboratory Validation						
Quizalofop-p-ethyl (BAS 9152 H)	49634805	49634807		Water <sup>1</sup>	10/03/2015	BASF	LC/MS/MS	0.001 mg/kg (ppm)
Quizalofop-p								
3-OH-Quizalofop-acid								

<sup>1</sup> Characterized drinking (tap) and surface (source not specified) water matrices were used for both the ECM validation and ILV (p. 20; Appendix 5, pp. 159-160 of MRID 49634805; p. 19; Appendix J, pp. 157-158 of MRID 49634807). The tap water used for the ILV was the same as that used in the ECM validation, while the surface water differed.

## I. Principle of the Method

Water (10 ± 0.1 g) was fortified with a mixed standard solution of quizalofop-p-ethyl (BAS 9152 H) and quizalofop-p in acetonitrile and 3-OH-quizalofop-acid in methanol for procedural recoveries (pp. 28, 31 of MRID 49634805). Characterized drinking (tap) water and surface water (source not specified) were used for the validation (p. 20; Appendix 5, pp. 159-160). Non-fortified water (10 ± 0.1 g) is weighed into a glass culture tube and combined with 0.1 mL of acetonitrile and 0.1 mL of methanol to equal the solution proportions of the fortified samples (p. 31). For quizalofop-p-ethyl and quizalofop-p analysis, a 0.051-mL aliquot of each sample (fortified or solvent adjusted non-fortified) is combined with 0.449 mL of acetonitrile and 0.5 mL of acetonitrile:water (90:10, v:v, S1), vortexed, and analyzed directly by LC/MS/MS (pp. 26, 32; Figure 1, p. 53). For 3-OH-quizalofop-acid analysis, a 0.051-mL aliquot of each sample is combined with 0.949 mL of acetonitrile:water (55:45, v:v, S2), vortexed, and analyzed directly by LC/MS/MS.

**LC/MS/MS of Quizalofop-p-ethyl (BAS 9152 H) and Quizalofop-p:** Samples are analyzed using a Waters UPLC Acquity system and an Applied Biosystems Sciex 5000 MS with electrospray ionization (ESI; p. 34 of MRID 49634805). The following LC conditions were used: Acquity UPLC BEH C18 column (2.1 mm x 50 mm, 1.7 µm, column temperature 50°C), mobile phase of (A) 4mM ammonium formate with 0.1% formic acid in water and (B) 4mM ammonium formate with 0.1% formic acid in methanol [percent A:B (v:v) at 0.0-0.5 min. 95:5, 1.0 min. 50:50, 3.0-3.5 min. 5:95, 3.6-4.0 min. 95:5], and injection volume of 20 µL. The following MS/MS conditions were used: positive ion mode and ionization temperature 500°C. Analytes are identified using two ion pair

transitions; one for quantitation (Q, "primary") and one for confirmation (C, "secondary"). Ion transitions monitored were as follows:  $m/z$  373→299 (Q) and  $m/z$  375→301 (C) for quizalofop-p-ethyl, and  $m/z$  345→299 (Q) and  $m/z$  345→100 (C) for quizalofop-p. Expected retention times are *ca.* 2.86 and 2.46 minutes for quizalofop-p-ethyl and quizalofop-p, respectively.

LC/MS/MS of 3-OH-Quizalofop-acid: Samples are analyzed using the same UPLC/MS/MS system as describe above (p. 35 of MRID 49634807). The following "primary" LC conditions were used: Acquity UPLC BEH Phenyl column (2.1 mm x 100 mm, 1.7  $\mu$ m, column temperature 50°C), mobile phase of (A) 4mM ammonium formate with 0.1% formic acid in water and (B) 4mM ammonium formate with 0.1% formic acid in methanol [percent A:B (v:v) at 0.0-0.5 min. 95:5, 3.0-3.5 min. 5:95, 3.6-4.0 min. 95:5], and injection volume of 30  $\mu$ L. The following MS/MS conditions were used: negative ion mode and ionization temperature 550°C. 3-OH-Quizalofop-acid is identified using a single ion pair transition:  $m/z$  359→166. Expected retention time is *ca.* 3.02 minutes. The following modification was made as a confirmatory "secondary" UPLC/MS/MS method: Acquity UPLC HSS T3 column (2.1 mm x 100 mm, 1.8  $\mu$ m), with all other conditions and expected retention time the same (p. 36).

ILV: Test compounds and two water matrices (tap and surface) were supplied by BASF (pp. 19-20 of MRID 49634807). Both water matrices were characterized (Appendix J, pp. 157-158). The tap water used for the ILV was the same as that used in the ECM validation, while the surface water (source not specified) differed (Appendix 5, pp. 158-159 of MRID 49634805). The independent laboratory performed the method as written with the following modifications: EPL deionized (DI) waster was used in place of study sample water to prepare reagent blanks; 10x LOQ fortifications of quizalofop-p-ethyl and quizalofop-p were diluted by a factor of 5 with acetonitrile:water (90:10, v:v, S1) and 10x LOQ fortifications of 3-OH-quizalofop-acid were diluted by a factor of 5 with acetonitrile:water (55:45, v:v, S2) prior to analysis; samples were analyzed using an Agilent 1290 HPLC system and an Applied Biosystems Sciex 6500 Q-Trap MS/MS with Turbo Ion Spray; injection volume was reduced to 20  $\mu$ L for 3-OH-quizalofop-acid analyses; and chromatographic run times were extended to 7.0 minutes for quizalofop-p-ethyl and quizalofop-p and 6.0 minutes for 3-OH-quizalofop-acid (pp. 21-27). Expected retention times were *ca.* 3.3, and 2.9 minutes for quizalofop-p-ethyl and quizalofop-p, respectively. For 3-OH-quizalofop-acid, expected retention times were *ca.* 3.15 and 3.3 minutes using the BEH Phenyl and HSS T3 columns, respectively.

LOQ and LOD: In the ECM and ILV, the LOQ and LOD were 0.001 mg/kg and 0.0002 mg/kg, respectively, for all three analytes (pp. 7, 45-46 of MRID 49634805; pp. 7, 33 of MRID 49634807).

## II. Recovery Findings

ECM (MRID 49634805): Mean recoveries and relative standard deviations (RSDs) were within guidelines (mean 70-120%; RSD  $\leq$ 20%) for analysis of quizalofop-p-ethyl (BAS 9152 H) and its transformation products quizalofop-p and 3-OH-quizalofop-acid in drinking (tap) water and surface (source not specified) water at fortification levels of 0.001 mg/kg (LOQ) and 0.01 mg/kg (10x LOQ; Tables 1-3, pp. 41-43). Quizalofop-p-ethyl and quizalofop-p were identified and quantified using two ion transitions, while 3-OH-quizalofop-acid was identified and quantified using two chromatographic methods; quantitation and confirmation recovery results were comparable. The water matrices were fully characterized by Agvise Laboratories, Northwood, North Dakota (Appendix 5, pp. 159-160).

ILV (MRID 49634807): Mean recoveries and relative standard deviations (RSDs) were within guidelines (mean 70-120%; RSD  $\leq$ 20%) for analysis of quizalofop-p-ethyl (BAS 9152 H) and its transformation products quizalofop-p and 3-OH-quizalofop-acid in drinking (tap) water and surface (source not specified) water at fortification levels of 0.001 mg/kg (LOQ) and 0.01 mg/kg (10x LOQ; corrected recoveries; Tables 1-6, pp. 30-32; Appendix H, pp. 129-147). Quizalofop-p-ethyl and quizalofop-p were identified and quantified using two ion transitions, and 3-OH-quizalofop-acid was identified and quantified using two chromatographic methods; quantitation and confirmation recovery results were comparable. The method was validated for quizalofop-p-ethyl at both fortification levels in the two water matrices after one trial and for quizalofop-p and 3-OH-quizalofop-acid after two trials, with minor method modifications and equivalent instrument substitutions (pp. 25, 29-30; Appendix H, pp. 129-147). The water matrices were fully characterized by Agvise Laboratories, Northwood, North Dakota (Appendix J, pp. 157-158).

**Table 2. Initial Validation Method Recoveries for Quizalofop-p-ethyl (BAS 9152 H) and Its Transformation Products Quizalofop-p and 3-OH-Quizalofop-acid in Water<sup>1</sup>**

Analyte	Fortification Level (mg/kg)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
<b>Drinking (Tap) Water</b>						
Quantitation						
Quizalofop-p-ethyl	0.001 (LOQ)	5	93.6-103	97.6	3.93	4.03
	0.01	5	82.5-97.1	91.7	6.05	6.60
Quizalofop-p	0.001 (LOQ)	5	84.0-122	103	17.4	16.9
	0.01	5	78.8-102	90.1	8.24	9.14
3-OH-Quizalofop-acid	0.001 (LOQ)	5	76.6-88.8	81.6	4.81	5.89
	0.01	5	73.5-81.1	79.0	3.17	4.02
Confirmation						
Quizalofop-p-ethyl	0.001 (LOQ)	5	88.6-99.0	93.7	4.10	4.38
	0.01	5	83.8-94.3	90.0	4.56	5.06
Quizalofop-p	0.001 (LOQ)	5	97.0-113	108	6.19	5.75
	0.01	5	78.0-106	92.8	12.4	13.4
3-OH-Quizalofop-acid	0.001 (LOQ)	5	71.0-98.2	82.5	11.0	13.4
	0.01	5	71.2-85.3	76.9	5.16	6.71
<b>Surface Water</b>						
Quantitation						
Quizalofop-p-ethyl	0.001 (LOQ)	5	94.4-104	99.6	3.82	3.84
	0.01	5	79.0-86.1	83.8	2.91	3.47
Quizalofop-p	0.001 (LOQ)	5	100-114	105	5.66	5.40
	0.01	5	89.3-102	96.5	5.36	5.55
3-OH-Quizalofop-acid	0.001 (LOQ)	5	86.0-126	101	16.1	16.0
	0.01	5	80.4-103	86.8	9.38	10.8
Confirmation						
Quizalofop-p-ethyl	0.001 (LOQ)	5	96.0-110	104	5.78	5.53
	0.01	5	81.5-86.3	84.1	2.28	2.71
Quizalofop-p	0.001 (LOQ)	5	106-119	112	5.49	4.90
	0.01	5	87.0-106	99.6	8.36	8.39
3-OH-Quizalofop-acid	0.001 (LOQ)	5	90.4-126	103	14.6	14.2
	0.01	5	77.6-88.9	80.9	4.64	5.73

Data (uncorrected recovery results; Appendix 6, pp. 164-175) were obtained from Tables 1-3, pp. 41-43 of MRID 49634805.

<sup>1</sup> Water characterizations were provided, but source location for the surface water was not reported (p. 20; Appendix 5, pp. 158-159).

**Table 3. Independent Validation Method Recoveries for Quizalofop-p-ethyl (BAS 9152 H) and Its Transformation Products Quizalofop-p and 3-OH-Quizalofop-acid in Water<sup>1</sup>**

Analyte	Fortification Level (mg/kg)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
<b>Drinking (Tap) Water</b>						
Quantitation						
Quizalofop-p-ethyl	0.001 (LOQ)	5	72.00-108.60	88.48	15.45	17.46
	0.01	5	86.70-113.30	98.26	10.10	10.28
Quizalofop-p	0.001 (LOQ)	5	82.40-107.00	93.48	9.91	10.60
	0.01	5	93.39-111.08	99.14	7.54	7.60
3-OH-Quizalofop-acid	0.001 (LOQ)	5	80.24-113.14	100.22	13.70	13.67
	0.01	5	108.72-119.75	114.01	4.16	3.65
Confirmation						
Quizalofop-p-ethyl	0.001 (LOQ)	5	67.60-109.00	84.56	16.84	19.92
	0.01	5	84.10-110.30	96.90	9.29	9.59
Quizalofop-p	0.001 (LOQ)	5	98.80-117.40	107.68	7.78	7.22
	0.01	5	100.40-123.82	110.93	8.83	7.96
3-OH-Quizalofop-acid	0.001 (LOQ)	5	110.33-126.58	116.99	7.16	6.12
	0.01	5	111.53-124.27	118.23	5.38	4.55
<b>Surface Water</b>						
Quantitation						
Quizalofop-p-ethyl	0.001 (LOQ)	5	79.60-128.20	113.24	19.60	17.31
	0.01	5	84.10-114.90	93.74	12.69	13.54
Quizalofop-p	0.001 (LOQ)	5	78.80-117.06	95.33	15.10	15.83
	0.01	5	102.82-110.50	108.40	3.16	2.92
3-OH-Quizalofop-acid	0.001 (LOQ)	5	75.43-108.73	87.02	13.57	15.59
	0.01	5	92.65-107.49	100.81	6.79	6.74
Confirmation						
Quizalofop-p-ethyl	0.001 (LOQ)	5	89.00-135.20	116.24	17.23	14.82
	0.01	5	80.80-118.40	94.14	14.71	15.62
Quizalofop-p	0.001 (LOQ)	5	83.80-126.80	108.20	15.51	14.33
	0.01	5	95.04-111.37	104.37	6.47	6.20
3-OH-Quizalofop-acid	0.001 (LOQ)	5	100.50-111.94	104.83	4.70	4.49
	0.01	5	99.97-109.50	105.07	4.13	3.93

Data (corrected recovery results; p. 29; Appendix H, pp. 129-147) were obtained from Tables 1-6, pp. 30-32 of MRID 49634807.

<sup>1</sup> The water matrices, supplied by BASF, were characterized, but source location for the surface water was not reported. (p. 19; Appendix 5, pp. 157-158).

### III. Method Characteristics

In the ECM, the LOQ in water was 0.001 mg/kg (ppm) for quizalofop-p-ethyl (BAS 9152 H) and its transformation products quizalofop-p and 3-OH-quizalofop-acid, equivalent to 0.05 ng/mL in the final sample extract solutions (pp. 7, 45-46 of MRID 49634805). The ECM defined the LOQ as the lowest fortification level successfully tested. The ECM defined the LOD as 20% of the LOQ, or 0.0002 mg/kg for all three analytes, equivalent to the lowest calibrant standard, 0.01 ng/mL, for each analyte. The lowest calibrant standards were reported as having good detectability (signal to noise ratio greater than 3:1; Appendix 4, pp. 74, 79, 84, 89, 94, 99). The ILV reported the same LOQ and LOD as the ECM (pp. 7, 33-34 of MRID 49634807).



**Table 4. Method Characteristics for Quizalofop-p-ethyl (BAS 9152 H) and Its Transformation Products Quizalofop-p and 3-OH-Quizalofop-acid in Water**

		Quizalofop-p-ethyl	Quizalofop-p	3-OH-Quizalofop-acid
Limit of Quantitation (LOQ)		0.001 mg/kg (ppm)		
Limit of Detection (LOD)		0.0002 mg/kg		
Linearity (calibration curve $r^2$ and concentration range) <sup>1</sup>	ECM:	Q ion: $r^2 = 0.9990-0.9998$ C ion: $r^2 = 0.9980-0.9990$	Q ion: $r^2 = \mathbf{0.9819}-0.9986$ C ion: $r^2 = \mathbf{0.9908}-0.9980$	Q LC-1: $r^2 = \mathbf{0.9886}-0.9978$ C LC-2: $r^2 = 0.9956-0.9958$
	Range:	0.01-0.2 ng/mL		
	ILV:	Q ion: $r^2 = 0.9986-0.9999$ C ion: $r^2 = 0.9972-0.9999$	Q ion: $r^2 = 0.9979-0.9993$ C ion: $r^2 = 0.9995-0.9999$	Q ion: $r^2 = \mathbf{0.9876}-0.9962$ C ion: $r^2 = \mathbf{0.9812}-\mathbf{0.9866}$
	Range:	0.01-1.0 ng/mL	0.01-1.0 ng/mL	0.0103-0.206 ng/mL
Repeatable	ECM:	Yes at LOQ and 10x LOQ. [drinking (tap) and surface (source not specified) water matrices] <sup>2</sup>		
	ILV:	Yes at LOQ and 10x LOQ. [drinking (tap) surface (source not specified) water matrices] <sup>2</sup>		
Reproducible		Yes.		
Specific	ECM:	No interferences (based on peak area) at analyte retention time in reagent blank and matrix controls.	No interferences (based on peak area) at analyte retention time in reagent blank and matrix controls, except for minor interferences (28-34% of LOD) in drinking water control using C ion analysis.	No interferences (based on peak area) at analyte retention time in reagent blank and matrix controls.
	ILV:	For Q ion, baseline noise was <i>ca.</i> 55% of LOD (0.01 ng/mL calibrant, based on peak height) at analyte retention time in the reagent blank and interferences were <i>ca.</i> 7-16% of LOD in the matrix controls. For C ion, baseline noise was <i>ca.</i> 8-20% of LOD in reagent blank and matrix controls.	For Q ion, peak of lowest calibrant (0.01 ng/mL, LOD) was not well resolved above baseline, with baseline noise <i>ca.</i> 25% of LOQ (0.05 ng/mL calibrant, based on peak height) at analyte retention time in reagent blank and matrix controls. For C ion, baseline noise in the reagent blank and matrix controls was <i>ca.</i> 30% of LOD.	For LC-1 (Q) and LC-2 (C), interferences (based on peak height) were <i>ca.</i> 5-30% of LOD at analyte retention time in reagent blank and matrix controls.

Data were obtained from pp. 7, 37, 44-46; Tables 1-3, pp. 41-43; Appendix 2, pp. 60-65; Appendix 3, pp. 67-72; Appendix 4, pp. 104-115, 128-139; Appendix 6, pp. 164-175 of MRID 49634805; pp. 7, 33-34; Appendix A, pp. 38-39, 41, 44-46; Appendix B, pp. 52-53, 59-61; Appendix C, pp. 67-68, 74-76; Appendix D, pp. 82-83, 89-91; Appendix E, pp. 97-98, 103-105; Appendix F, pp. 111-112, 117-119; Appendix H, pp. 129-147 of MRID 49634807.

Linearity is satisfactory when  $r^2 \geq 0.995$ .

1 Linear regression with 1/x weighting (p. 37; Appendix 2, pp. 60-65 of MRID 49634805; Appendix A, p. 38; Appendix B, p. 52; Appendix C, p. 67; Appendix D, p. 82; Appendix E, p. 97; Appendix F, p. 111 of MRID 49634807). ECM coefficient of determination ( $r^2$ ) values are reviewer-generated from reported correlation coefficient (r) values (Appendix 6, pp. 164-175 of MRID 49634805; DER Attachment 2).

2 Water characterizations were provided, but source locations for surface waters were not reported (p. 20; Appendix 5, pp. 159-160 of MRID 49634805; p. 19; Appendix J, pp. 157-158 of MRID 49634807). Water matrices for ILV supplied by BASF. The tap water used for the ILV was the same as that used in the ECM validation, while the surface water differed.

#### IV. Method Deficiencies and Reviewer's Comments

1. For the ILV, the study author reported recovery ranges, means, standard deviations and relative standard deviations for each analyte/matrix/fortification level, but not all individual replicate recoveries (Tables 1-6, pp. 30-32 of MRID 49634807). All individual method recoveries should have been presented in the study report in tabular form. The reviewer calculated recoveries using the provided equations and raw data, without correction for residues found in the control samples (p. 29; Appendix H, pp. 129-147; DER Attachment 2). While there were discrepancies between the corrected recoveries presented in Tables 1-6 and the uncorrected recoveries calculated by the reviewer (Microsoft Excel v. 14.0.7153.5000), the discrepancies were <10% and considered most likely due to rounding and correction for controls (pp. 28-29).
2. The determination of the LOQ and LOD were not based on scientifically acceptable procedures as defined in 40 CFR Part 136, Appendix B. The ECM defined the LOQ as the lowest fortification level successfully tested (p. 7, 46 of MRID 49634805). The ECM defined the LOD as 20% of the LOQ, equivalent to the lowest calibrant standard, 0.01 ng/mL, for each analyte. The lowest calibrant standard was reported as having good detectability (signal to noise ratio greater than 3:1; Appendix 4, pp. 74, 79, 84, 89, 94, 99). The ILV reported the same LOQ and LOD as the ECM (pp. 7, 33-34 of MRID 49634807). Detection limits should not be based on the arbitrarily selected lowest concentration in the spiked samples. Additionally, the lowest toxicological level of concern in water was not reported. A LOQ above toxicological levels of concern results in an unacceptable method classification.
3. For the ILV, chromatograms of quizalofop-p-ethyl using the quantitation ion show baseline noise was *ca.* 55% of LOD (0.01 ng/mL calibrant, based on peak height) at the analyte retention time in the reagent blank and interferences were *ca.* 7-16% of LOD in the matrix controls (Appendix C, pp. 68, 74-76 of MRID 49634807). For confirmation ion analysis, baseline noise was *ca.* 8-20% of LOD in reagent blank and matrix controls (Appendix D, pp. 83, 89-91).

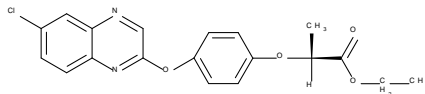
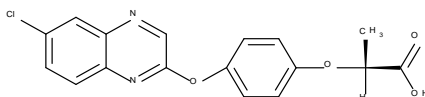
Chromatograms for quizalofop-p using the quantitation ion show the peak of the lowest calibrant (0.01 ng/mL, LOD) is not well resolved above baseline, with baseline noise *ca.* 25% of LOQ (0.05 ng/mL calibrant, based on peak height) at the analyte retention time in the reagent blank and matrix controls (Appendix A, p. 39 of MRID 49634807). For the confirmation ion, baseline noise in the reagent blank and matrix controls was *ca.* 30% of LOD (Appendix B, pp. 53, 59-61).

4. In both the ECM validation and ILV, the linearity of the quizalofop-p (quantitation and confirmation ions) and 3-OH-quizalofop-acid (LC-1 quantitation method) calibration standard curves was not always satisfactory ( $r^2 \geq 0.995$ ; (Appendix H, pp. 130, 134, 136, 141 of MRID 49634807; DER Attachment 2).
5. In the ILV, sample recoveries were corrected for residues found in the controls (p. 29; Appendix H, pp. 129-147 of MRID 49634807). The final recovery was listed as "Corrected Recovery (%)" in the raw data tables.

6. For the ILV, an initial trial was run using the three analytes, drinking and surface water matrices (Sets V001 and V002), and polypropylene centrifuge tubes in place of the method specified glass culture tubes (Appendix I, pp. 150-151, 154 of MRID 49634807). Recoveries of quizalofop-p and 3-OH-quizalofop-acid were reported as acceptable, while recoveries of quizalofop-p-ethyl were low (*ca.* 50%). BASF rejected this trial because the method was not performed as written and the subsequent trial (Sets V001R for surface water and V002R for drinking water) using glass culture tubes was considered the first ILV attempt (Appendix H, pp. 129, 131, 133, 135, 137-141, 143, 145).
7. For both the ECM validation and ILV, the source locations for the surface water matrices were not reported (p. 20 of MRID 49634805; p. 19 of MRID 49634807).
8. The equipment substitutions and method modifications implemented by the independent laboratory (see section **I. Principle of the Method, ILV**; above for details) are not considered substantial changes to the ECM.
9. As part of the ECM validation, it was determined that under refrigerator storage water sample extract and final solutions were stable for 7 days (pp. 8, 23, 44; Appendix 1, pp. 55-58 of MRID 49634805).
10. The following typographical errors were noted in the ECM study report: Figure 4.6 (Appendix 4, p. 103 of MRID 49634805), "Standard Concentration: **0.02** ng/mL" should read Standard Concentration: 0.2 ng/mL, and in section **2.2 Test and Reference Items** (pp. 21-22), "-chloroquinoxanlin-" should read -chloroquinoxalin-.
11. It was reported for the ILV that a set of thirteen samples (one reagent blank, two matrix controls, and ten fortified samples) required *ca.* 12-14 work hours, which included calculation of the results (p. 33 of MRID 49634807).

## V. References

- U.S. Environmental Protection Agency. 2012. Ecological Effects Test Guidelines, OCSPP 850.6100, Environmental Chemistry Methods and Associated Independent Laboratory Validation. Office of Chemical Safety and Pollution Prevention, Washington, DC. EPA 712-C-001.
- 40 CFR Part 136. Appendix B. Definition and Procedure for the Determination of the Method Detection Limit-Revision 1.11, pp. 317-319.

**Attachment 1: Chemical Names and Structures****Quizalofop-p-ethyl (QPE, BAS 9152 H, D(+))NC-302)****IUPAC Name:** Ethyl (2R)-2-[4-(6-chloroquinoxalin-2-yloxy)phenoxy]propionate**CAS Name:** Ethyl (2R)-2-[4-[(6-chloro-2-quinoxalinyloxy]phenoxy]propanoate**CAS Number:** 100646-51-3**SMILES String:** n1c2ccc(Cl)cc2ncc1Oc3ccc(OC(C)C(=O)OCC)cc3**Quizalofop-p (QP, R-QA, 302D-ACID)****IUPAC Name:** (R)-2-[4-(6-chloroquinoxalin-2-yloxy)phenoxy]propionic acid**CAS Name:** (2R)-2-[4-[(6-chloro-2-quinoxalinyloxy]phenoxy]propanoic acid**CAS Number:** 94051-08-8**SMILES String:** n1c2ccc(Cl)cc2ncc1Oc3ccc(OC(C)C(=O)O)cc3**3-OH-Quizalofop-acid (3-OH-QA, R-3-OH-QA, R(+)-3-OH-quizalofop-acid)****IUPAC Name:** (2S)-2-[4-(6-chloro-3-hydroxyquinoxalin-2-yl)oxyphenoxy]propanoic acid**CAS Name:** (R)-2-[4-(6-Chloro-3-hydroxyquinoxalin-2-yloxy)phenoxy]propionic acid**CAS Number:** Not available.**SMILES String:** [H]C(C)(C(=O)O)Oc1ccc(cc1)Oc2c(nc3cc(O)ccc3n2)Cl)O