

**Test Material:** Tefluthrin

**MRID:** 49394206

**Title:** Tefluthrin: Tefluthrin – Analytical Method (GRM002.09A) for the Determination of Tefluthrin in Surface Water by GC/MSD – Analytical Method

**MRID:** 49648103

**Title:** Tefluthrin: Tefluthrin – Independent Laboratory Validation of Analytical Method (GRM002.09A) for the Determination of Tefluthrin in Surface Water by GC-MSD – Final ILV Report

**EPA PC Code:** 128912

**OCSPP Guideline:** 850.6100

**For CDM Smith**

**Primary Reviewer:** Lisa Muto

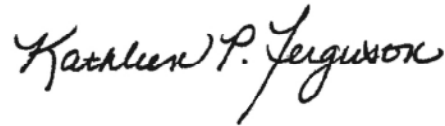
**Signature:**



**Date:** 11/10/15

**Secondary Reviewer:** Kathleen Ferguson

**Signature:**



**Date:** 11/10/15

**QC/QA Manager:** Joan Gaidos

**Signature:**



**Date:** 11/10/15

**Analytical method for tefluthrin and its Z-isomer R230310 in water**

**Reports:** ECM: EPA MRID No.: 49394206. Mayer, L.C. 2014. Tefluthrin: Tefluthrin – Analytical Method (GRM002.09A) for the Determination of Tefluthrin in Surface Water by GC/MSD – Analytical Method. Report No.: GRM002.09A. Task No.: TK00225186. Report prepared, sponsored and submitted by Syngenta Crop Protection, LLC, Greensboro, North Carolina; 41 pages. Final report issued May 9, 2014.  
ILV: EPA MRID No. 49648103. Guo, D. 2015. Tefluthrin: Tefluthrin – Independent Laboratory Validation of Analytical Method (GRM002.09A) for the Determination of Tefluthrin in Surface Water by GC-MSD – Final ILV Report. Report No: PASC-REP-0628. PASC Project No.: 141-1145. Task No.: TK00259746. Report prepared by Primera Analytical Solutions Corp., Princeton, New Jersey, sponsored and submitted by Syngenta Crop Protection, LLC, Greensboro, North Carolina; 87 pages. Final report issued May 12, 2015.

**Document No.:** MRIDs 49394206 & 49648103


**Guideline:** 850.6100

**Statements:** ECM: The study was conducted with no claim of compliance with USEPA or OECD Good Laboratory Practice (GLP) standards (p. 3 of MRID 49394206). Signed and dated No Data Confidentiality and GLP statements were provided (pp. 2-3). Quality Assurance and Authenticity statements were not provided.  
ILV: The study was conducted in compliance with USEPA GLP standards (p. 3 of MRID 49648103). Signed and dated No Data Confidentiality, GLP, and Quality Assurance statements were provided (pp. 2-4). A statement of the authenticity of the study report was not included.

**Classification:** This analytical method is classified as unacceptable but upgradable upon addressing the following issues: It could not be determined if the ECM and ILV were performed by different laboratories, The ECM was summary report of another study; the ECM lacked important data, such as the performing laboratory name/address, matrix characterization, and individual recovery data, The determinations of the LOQ and LOD were not shown to be based on scientifically acceptable procedures, The ECM and ILV calibration curves did not adequately bracket the instrumental response at the LOQ.

**PC Code:** 128912

**Reviewer:** Ibrahim Abdel-Saheb, Ph.D.  
Environmental Scientist  
US EPA

**Signature:**   
**Date:** 6-27-2016

## Executive Summary

This analytical method, Syngenta Analytical Method (GRM002.09A), is designed for the quantitative determination of tefluthrin in surface water using GC/MS. The method is quantitative for tefluthrin at the stated LOQ of 0.10 µg/L. The independent laboratory validated the method after one trial; however, the laboratory which performed the ECM was not reported, so it could not be determined if the ECM and ILV were performed by different laboratories. The surface water matrix was fully characterized in the ILV, but not in the ECM. Tefluthrin was identified with three ions; however, recovery data was provided for only one ion, *m/z* 241, in the ECM and ILV.

**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						
Tefluthrin	49394206 <sup>1</sup>	49648103		Surface water <sup>2,3</sup>	09/05/2014	Syngenta	GC/MS	0.10 µg/L (0.1 ppb)

1 Data provided in the ECM MRID 49394206 study report was summarized from another study, TK0225184 (pp. 19, 22; see Reviewer's Comment #1).

2 In the ECM, the surface water was not characterized or described. The water source was not specified.

3 In the ILV, the surface water (RIMV00115-0001 Julian Surface Water) was fully characterized by Agvise Laboratories, Inc., Northwood, North Dakota (p. 10; Table 1, p. 16 of MRID 49648103).

## I. Principle of the Method

Samples (100 mL) of water in 250-mL nalgene bottles were fortified, as necessary, and extracted with 20 mL of toluene via shaking for 15 minutes (p. 12; Appendix 3, p. 41 of MRID 49394206). After centrifugation (3500 rpm for 5 minutes), and aliquot (1.0 mL) of the top layer (toluene layer) was diluted if necessary and analyzed directly using GC/MS.

Optional SPE Procedure: Samples (100 mL) of water in 250-mL nalgene bottles were fortified, as necessary, and extracted using a solid phase extraction column procedure (pp. 12-13; Appendix 1, p. 39; Appendix 3, p. 41 of MRID 49394206). An individual Oasis HLB cartridge (6 cc, 150 mg) was used for each sample. The SPE column was pre-conditioned with toluene, methanol and ultra-pure water (5 mL each) under gravity or vacuum to achieve a rate of *ca.* 1 mL/min. (cartridges should not be allowed to become dry). The treated water samples were applied to the column at a rate of *ca.* 10 mL/min. (cartridges should not be allowed to become dry). The empty sample container was rinsed with 5 mL of ultra-pure water, and the rinsing was added to the column. After that rinsing was passed through the column, the column was dried under vacuum for 15 minutes. The empty sample containers were charged with 1 g of anhydrous sodium sulfate and 5 g of toluene. This mixture was added to the SPE column (*ca.* 1-2 mL.min. flow). Elution of the tefluthrin was continued with an additional 5 mL of toluene (under high vacuum). The eluate final volume was adjusted to 10 mL with toluene. An aliquot (0.5 mL) was combined with 0.5 mL of toluene in an autosampler vial for analysis by GC/MS (further dilution prior to GC/MS analysis was performed as necessary).

Samples were analyzed for tefluthrin by a Hewlett Packard 6890 GC system with a Hewlett Packard 5973 detector (pp. 14-15; Appendix 1, p. 39 of MRID 49394206). The following instrumental conditions were employed: HP-5MS column (30.0 m x 0.25 mm i.d.), splitless-carbofrit liner (4 mm) injection port, injector temperature 275°C, helium carrier gas (1.0 mL/min.), temperature program 150°C at 1 min. to 300°C at 2 min., and negative chemical (SIM) ionization mode. Injection volume was 2 µL. Tefluthrin was identified and quantified using two ion transitions, primary and confirmatory. Ions monitored were  $m/z$  241,  $m/z$  243 and  $m/z$  205 (ion ratio, 100:33:13) for tefluthrin. The retention time for tefluthrin was *ca.* 5.1 minutes. No further confirmation was performed.

The ILV was performed exactly as above using a GC6890 GC system with a MSD5973 (pp. 11; Appendix 1, p. 36 of MRID 49648103). No significant modifications to the ECM were implemented. Ions monitored were  $m/z$  241,  $m/z$  243 and  $m/z$  205 (Figures 10-11, pp. 29-30). The retention time was *ca.* 5.5 minutes.

The LOQ for tefluthrin was 0.10 µg/L (0.10 ppb) in the ECM and ILV (pp. 18-19 of MRID 49394206; pp. 11-12 of MRID 49648103). In the ECM, the LOD was reported as 0.25 pg, equivalent to 0.125 pg/µL when using a 2 µL injection volume. In the ILV, the LOD was reported as 0.50 pg, equivalent to 0.25 pg/µL when using a 2 µL injection volume.

## II. Recovery Findings

ECM (MRID 49394206): Mean recoveries and relative standard deviations (RSDs) were within guideline requirements (mean 70-120%; RSD ≤20%) for analysis of tefluthrin in surface water at fortification levels of 0.10 µg/L (LOQ) and 1.0 µg/L (10×LOQ); however, individual recovery data was not provided (p. 19). Tefluthrin was identified using three ions; however, only one ion was used for quantification (pp. 14-15, 19). The method calculations allowed for the correction of recoveries for residues quantified in the controls; however, none were quantified (pp. 15-16; Figures 10-11, pp. 33-34). The surface water matrix was not characterized or described. Data provided in the study report was summarized from another study, TK0225184 (pp. 19, 22; see Reviewer's Comment #1).

ILV (MRID 49648103): Mean recoveries and relative standard deviations (RSDs) were within guideline requirements (mean 70-120%; RSD ≤20%) for analysis of tefluthrin in surface water at fortification levels of 0.10 µg/L (LOQ) and 1.0 µg/L (10×LOQ; pp. 12-13; Table 3, p. 18). Tefluthrin was identified using three ions; however, only one ion was used for quantification (pp. 12-13; Table 3, p. 18; Figures 10-11, pp. 29-30). The method calculations allowed for the correction of recoveries for residues quantified in the controls; however, none were quantified (Figures 8-9, pp. 27-28; Appendix 1, pp. 56-57; Appendix 3, p. 87). The method was validated after one trial (p. 8). The surface water (RIMV00115-0001 Julian Surface Water) was fully characterized (p. 10; Table 1, p. 16).

**Table 2. Initial Validation Method Recoveries for Tefluthrin in Surface Water<sup>1,2</sup>**

Analyte	Fortification Level (µg/L)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
Primary ion ( <i>m/z</i> 241)						
Tefluthrin	0.10 (LOQ)	5	90-13	97	5	5
	1.0	5	92-97	94	2	2

Data (uncorrected recovery results; pp. 15-16; Figures 10-11, pp. 33-34) were obtained from p. 19 of MRID 49394206.

1 The surface water was not characterized or described. The water source was not specified.

2 Ions monitored were *m/z* 241, *m/z* 243 and *m/z* 205 (pp. 14-15); however, only recovery data for the *m/z* 241 ion was reported in the study report (p. 19).

**Table 3. Independent Validation Method Recoveries for Tefluthrin in Surface Water<sup>1,2</sup>**

Analyte	Fortification Level (µg/L)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
Primary ion ( <i>m/z</i> 241)						
Tefluthrin	0.10 (LOQ)	5	81-96	85	6	7
	1.0	5	100-104	103	2	2

Data (uncorrected recovery results; Figures 8-9, pp. 27-28; Appendix 1, pp. 56-57; Appendix 3, p. 87) were obtained from pp. 12-13; Table 3, p. 18 of MRID 49648103.

1 The surface water (RIMV00115-0001 Julian Surface Water) was fully characterized by Agvise Laboratories, Inc., Northwood, North Dakota (p. 10; Table 1, p. 16).

2 Ions monitored were *m/z* 241, *m/z* 243 and *m/z* 205 (Figures 10-11, pp. 29-30); however, only recovery data for the *m/z* 241 ion was reported in the study report (pp. 12-13; Table 3, p. 18).

### III. Method Characteristics

The LOQ for tefluthrin was 0.10 µg/L (0.10 ppb) in the ECM and ILV (pp. 18-19 of MRID 49394206; pp. 11-12 of MRID 49648103). In the ECM and ILV, the LOQ was defined as the lowest analyte concentration in a sample at which the method has been validated. The ECM study author also advised that the response for the analyte peak should be no less than four times the mean amplitude of the background noise at the analyte retention time in the control sample. In the ECM, the LOD was reported as 0.25 pg, equivalent to 0.125 pg/µL when using a 2 µL injection volume. In the ILV, the LOD was reported as 0.50 pg, equivalent to 0.25 pg/µL when using a 2 µL injection volume; this value corresponded to the lowest calibration standard. In the ECM and ILV, the LOD was defined as the lowest analyte concentration which can be detected above the mean amplitude of the background noise at the analyte retention time in the control sample. The ECM and ILV study authors also noted that the LOD can be estimated as three times the background noise and will vary between instruments and analytical runs. No calculations of the LOQ and LOD were reported in the ECM and ILV.

**Table 4. Method Characteristics**

		<b>Tefluthrin</b>
Limit of Quantitation (LOQ)		0.10 µg/L
Limit of Detection (LOD)	ECM	0.25 pg, equivalent to 0.125 pg/µL when using a 2 µL injection volume
	ILV	0.50 pg, equivalent to 0.25 pg/µL when using a 2 µL injection volume
Linearity (calibration curve $r^2$ and concentration range)	ECM <sup>1</sup>	$r^2 = 1.000$ ( $m/z$ 241)
	ILV <sup>1</sup>	$r^2 = 0.9999$ ( $m/z$ 241)
	Concentration range	0.25 pg/µL to 25 pg/µL (0.5 pg to 50.0 pg)
Repeatable	ECM <sup>1</sup>	Yes at LOQ and 10×LOQ ( $m/z$ 241). However, surface water was not characterized, and individual recovery data was not provided.
	ILV <sup>1</sup>	Yes at LOQ and 10×LOQ ( $m/z$ 241). Surface water fully characterized.
Reproducible		Yes at LOQ and 10×LOQ.
Specific	ECM	Matrix interferences were not observed. Identified using three ions; however, only one ion was used for quantification. <sup>2</sup>
	ILV	

Data were obtained from pp. 18-19; Figures 9-14, pp. 32-37 of MRID 49394206; pp. 11-13; Table 3, p. 18; Figures 7-12, pp. 26-31 of MRID 49648103.

<sup>1</sup> Data for the confirmatory ions  $m/z$  243 and  $m/z$  205 was not provided.

<sup>2</sup> A confirmatory method is not usually required when LC/MS and GC/MS is the primary method.

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

- It could not be determined if the ECM and ILV were performed by different laboratories. The ECM MRID 49394206 was a summary of data performed in another ILV: Underwood, T. 2014. Independent Laboratory Validation of Analytical Method (GRM002.09A) for the Determination of Tefluthrin in Surface Water by GC/MSD. TK0225184 (pp. 19, 22 of MRID 49394206). The ILV laboratory which performed TK0225184 was not reported in the ECM MRID 49394206, so it could not be determined if the data presented in the ECM was performed by a laboratory which differed from that of the ILV: Primera Analytical Solutions Corp. OCSPP guidelines state that the laboratory which performed the ILV must be independent of the laboratory which performed the ECM.

Additionally, in the summary report ECM MRID 49394206, the surface water matrix was not described, the individual recovery values were not reported, and the recovery data was only reported for one ion,  $m/z$  241. It is not certain if that missing information would have been in the original report ILV TK0225184.

2. The determinations of the LOQ and LOD were not based on scientifically acceptable procedures. In the ECM and ILV, the LOQ (0.1 µg/L, ppb) was defined as the lowest analyte concentration in a sample at which the method has been validated (pp. 18-19 of MRID 49394206; pp. 11-12 of MRID 49648103). The ECM study author also advised that the response for the analyte peak should be no less than four times the mean amplitude of the background noise at the analyte retention time in the control sample. The LOD was reported as 0.25 pg and 0.50 pg, respectively, in the ECM and ILV. In the ECM and ILV, the LOD was defined as the lowest analyte concentration which can be detected above the mean amplitude of the background noise at the analyte retention time in the control sample. The ECM and ILV study authors also noted that the LOD can be estimated as three times the background noise and will vary between instruments and analytical runs. No calculations of the LOQ and LOD were reported in the ECM and ILV.

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. An LOQ above toxicological levels of concern results in an unacceptable method classification.

The LOD differed between the ECM and ILV (pp. 18-19 of MRID 49394206; pp. 11-12 of MRID 49648103). In the ECM, the LOD was reported as 0.25 pg, equivalent to 0.125 pg/µL when using a 2 µL injection volume. In the ILV, the LOD was reported as 0.50 pg, equivalent to 0.25 pg/µL when using a 2 µL injection volume; this value corresponded to the lowest calibration standard.

3. The calibration curves did not adequately bracket the instrumental response at the LOQ. In the ECM, the lowest calibrants 0.25 µg/L and 0.50 µg/L yielded *m/z* 241 instrumental responses of 31 and 54, while the LOQ (0.10 µg/L) yielded an *m/z* 241 instrument response of 52 (Figures 2-3, pp. 25-26; Figure 12, p. 35 of MRID 49394206). In the ILV, the lowest calibrants 0.25 µg/L and 0.50 µg/L yielded *m/z* 241 instrumental responses of 1848.155 and 3681.86, while the LOQ (0.10 µg/L) yielded an *m/z* 241 instrument response of 2436.27 (Figures 1-2, pp. 20-21; Figure 10, p. 29 of MRID 49648103). For accuracy of calculations at the LOQ based on the calibration curve, at least two calibration standards should generate instrumental responses below and above the instrument response at the LOQ.
4. The data for confirmatory ions was not reported in the ECM and ILV; however, GC chromatograms of the confirmatory ions were provided (Figures 9-14, pp. 32-37 of MRID 49394206; pp. 11-13; Table 3, p. 18; Figures 7-12, pp. 26-31 of MRID 49648103). A confirmatory method is not usually required when LC/MS and GC/MS is the primary method.
5. The reviewer noted two typographical errors in the ECM (MRID 49394206): the GC column dimensions were incorrectly reported as “30m x0.25 m” in Appendix 1, p. 39, instead of “30.0m x 0.25 mm i.d.” on p. 14; and the flow-chart form of the analytical method was incorrectly referenced as “Appendix 4” on p. 12, instead of Appendix 3.
6. The ECM study author noted that the method could be applied to other water types (p. 20 of MRID 49394206). No chromatograms or data from water types other than surface were included in the report.

7. The ILV study author reported that communications between the independent laboratory and Syngenta study monitors were not necessary (p. 13 of MRID 49648103).
8. In the ECM, no significant matrix effects were found (pp. 18, 20 of MRID 49394206). Non-matrix matched standards were advised for quantification. Final extract stability was also assessed in the ECM. Final water samples in toluene were found to be stable for at least 10 days at *ca.* 4°C. This information was not supported by tabular data; this raw data may be contained in the original report TK0225184.
9. It was reported in the ECM that one analyst could complete one or two batches of 15 samples in 8 hours (one working day; p. 13 of MRID 49648103). The time for analysis was not reported in the ILV.

## 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****Tefluthrin (ICI993; ASF611; CGA221149; R151993; PP993; TFN; Force)**

- IUPAC Name:** 2,3,5,6-Tetrafluoro-4-methylbenzyl (1RS,3RS)-3-[(Z)-2-chloro-3,3,3-trifluoroprop-1-enyl]-2,2-dimethylcyclopropanecarboxylate.  
 2,3,5,6-Tetrafluoro-4-methylbenzyl (1RS)-cis-3-[(Z)-2-chloro-3,3,3-trifluoroprop-1-enyl]-2,2-dimethylcyclopropanecarboxylate.  
 2,3,5,6-Tetrafluoro-4-methylbenzyl (Z)-(1RS)-cis-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate.  
 2,3,5,6-Tetrafluoro-4-methylbenzyl cis-3-(Z-2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate.  
 3-(2-chloro-3,3,3-trifluoro-propenyl)-2,2-dimethyl-cyclopropanecarboxylic acid tetrafluoro-methyl-benzyl ester.
- CAS Name:** (2,3,5,6-Tetrafluoro-4-methylphenyl)methyl (1R,3R)-rel-3-[(1Z)-2-chloro-3,3,3-trifluoro-1-propenyl]-2,2-dimethylcyclopropanecarboxylate.  
 2,3,5,6-Tetrafluoro-4-methylbenzyl (Z)-(1RS)-cis-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate.  
 Cyclopropanecarboxylic acid, 3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethyl-, (2,3,5,6-tetrafluoro-4-methylphenyl) methyl ester, (1-alpha,3-alpha(Z))-(+)-.
- CAS Number:** 79538-32-2.
- SMILES String:** Cc2c(F)c(F)c(COC(=O)C1C(C=C(Cl)C(F)(F)F)C1(C)C)c(F)c2F

