

**Analytical method for carfentrazone-ethyl (F8426) and its transformation products F8426-benzoic acid (F8426-BAC), F8426-propionic acid (F8426-PAC), F8426-chloropropionic acid (F8426-Cl-PAC), and F8426-cinnamic acid (F8426-CAC) in soil**

**Reports:** ECM: MRID 44165040. Jang, D. 1996. Analytical Methodology for The Determination of Carfentrazone-ethyl (F8426) and Its Metabolites in/on Bare Soil. Report prepared, sponsored, and submitted by FMC Corporation, Richmond, California; 101 pages. FMC Study No.: 842E4194E1 and Report No.: RAN-0270M (pp. 1, 3). Final report issued August 19, 1996 (p. 3).  
ILV: MRID 49559801. Fitzpatrick, T. 2015. Independent Laboratory Validation for the Determination of Carfentrazone-ethyl (F8426) and its Metabolites in Soil by GC-MS. Report prepared by Primera Analytical Solutions Corp. (PASC), Princeton, New Jersey, sponsored and submitted by FMC Corporation, Ewing, New Jersey; 62 pages. PASC Project No.: 058-1095 and Report No.: PASC-REP-0557. FMC Study No.: 2014AMT-CFZ1651 and Report No.: PC-0854. Final report issued January 22, 2015.

**Document No.:** MRIDs 44165040 & 49559801

**Guideline:** 850.6100

**Statements:** ECM: The study was conducted in compliance with USEPA Good Laboratory Practice (GLP) standards (p. 3 of MRID 44165040). Signed and dated Data Confidentiality, GLP, Quality Assurance, and Authenticity Certification statements were provided (pp. 2-4, 27).  
ILV: The study was conducted in compliance with USEPA GLP standards (p. 3 of MRID 49559801). 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**. However, the registrant did not verify that the independent laboratory was provided with a soil of the most difficult analytical sample condition to analyze to demonstrate how well the method performs. Any communication between the independent laboratory and the study sponsor was not reported. The determinations of the LOQ and LOD were not based on scientifically acceptable procedures. For the ILV, linearity of the F8426-BAC, F8426-Cl-PAC, and F8426-CAC standard curves was not satisfactory.

**PC Code:** 128712

**Reviewer:** Gregory Orrick, Environmental Scientist  
U.S. Environmental Protection Agency

**Signature:**  
**Date:** May 19, 2015

**Executive Summary**

This analytical method, RAN-0270M, is designed for the quantitative determination of carfentrazone-ethyl (F8426) and its transformation products F8426-benzoic acid (F8426-BAC), F8426-propionic acid (F8426-PAC), F8426-chloropropionic acid (F8426-Cl-PAC), and F8426-cinnamic acid (F8426-CAC) in soil using GC/MS. The method is quantitative for the analytes at the stated LOQ of 5 µg/kg (ppb). The LOQ is approximately equal to the lowest toxicological level of concern in soil (4.5 µg/kg). The independent laboratory validated the method for analysis of carfentrazone-ethyl, F8426-PAC, and F8426-Cl-PAC in loamy sand soil at the LOQ and 10x LOQ after one trial, and for F8426-BAC and F8426-CAC after two additional GC/MS analyses using the

original final soil extracts. No major modifications were made by the independent laboratory. The loamy sand soil (7% clay, 0.39% organic carbon) used in the ILV, and supplied by FMC, may not have been of an equivalent, or more difficult, analytical sample condition as the sand and silt loam soils (uncharacterized) used for the ECM validation.

**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						
Carfentrazone-ethyl (F8426)	44165040	49559801		Soil <sup>1</sup>	19/08/1996	FMC Corporation	GC/MS	5 µg/kg (ppb)
F8426-BAc								
F8426-PAc								
F8426-Cl-PAc								
F8426-CAc								

<sup>1</sup> A loamy sand soil (7% clay, 0.39% organic carbon) was used in the ILV (Attachment II, Figure 15, p. 50 of MRID 49559801). Sand and silt loam soils (uncharacterized) were used in the ECM validation (p. 11 of MRID 44165040).

## I. Principle of the Method

Soil was fortified with a mixed standard solution of carfentrazone-ethyl (F8426), F8426-BAc, F8426-PAc, F8426-Cl-PAc, and F8426-CAc in acetonitrile for procedural recoveries (pp. 16, 20; Table 7, p. 73 of MRID 44165040). Control soil samples from two terrestrial field dissipation studies conducted in Finney County, Kansas (sand soil), and Polk County, Minnesota (silt loam soil), were used for validation (p. 11).

Diazomethane solution is prepared using potassium hydroxide, Carbitol<sup>®</sup>, ether, and Diazald<sup>®</sup> (pp. 13, 15-16). Soil samples (80 g) are reflux extracted with 200 mL of acetonitrile:water (8:2, v:v) for 1 hour using either occasional manual swirling or magnetic stir bars to mix (Figure 1, p. 10; pp. 16-18). Following cooling (*ca.* 15 minutes), the sample is vacuum filtered (Büchner funnel, Whatman GF/A filter paper). The filtrate is concentrated by rotary evaporation (*ca.* 50-60°C) to *ca.* 30 mL to remove solvent; 2-4 drops of Antifoam B<sup>®</sup> may be added to reduce flashing. The remaining aqueous sample is brought to *ca.* 50 mL with deionized water, acidified with 1 mL of 10% sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), and partitioned twice with methylene chloride (75 mL x 2) in the presence of sodium chloride (NaCl, *ca.* 1-2 teaspoons). Organic phases are passed through anhydrous sodium sulfate and glass wool, combined, and brought to volume (*ca.* 160 mL) with methylene chloride. Extract samples should be transferred to amber glass, screw-cap bottles to prevent photodegradation of the analytes. An aliquot (40 mL, or 20 g soil equivalent) of the extract is taken just to dryness under a nitrogen stream on a steam table (*ca.* 60-70°C). The resulting residues are reconstituted with ethyl ether (5 mL) and diazomethane solution (1 mL; preparation described on pp. 15-16) and allowed to derivatize for 30 minutes. Hexane (10 mL) is added to the derivatized sample, the sample is concentrated to *ca.* 1-2 mL under a nitrogen stream (*ca.* 60-70°C), then diluted with hexane (10 mL). The sample is applied to a Varian SI silica gel (1 g/6 mL) solid phase extraction (SPE) cartridge preconditioned with hexane. The loaded SPE cartridge is rinsed with hexane:ethyl acetate (95:5, v:v), then analytes are eluted with 10 mL of hexane:ethyl acetate (8:2, v:v). The eluate is concentrated to <0.5 mL under a nitrogen stream, then brought to volume (0.5 mL) with ethyl acetate for analysis. Matrix matched standards should be prepared (p. 19).

Samples were analyzed using an Hewlett-Packard (HP) 5890 GC system with an HP 5972 MSD operated in selected ion monitoring (SIM) mode (pp. 19, 22; Appendix A, p. 75; Appendix B, Figures 4-28, pp. 77-101 of MRID 44165040). The following GC conditions were used: Hewlett-Packard HP-5 5% Phenyl Methyl Crosslinked Silicone column (0.32 mm x 20-25 m, df = 0.52  $\mu$ m, injector temperature 250°C), temperature program [150°C (hold for 1 min.), 25°C/min. to 250°C, 5°C/min. to 260°C (hold for 4 min.), 30°C/min. to 295°C (hold for 2.75 min.)], and injection volume of 2  $\mu$ L. The following ions were monitored:  $m/z$  312 or 330 for carfentrazone-ethyl (F8426),  $m/z$  335 for F8426-BAC,  $m/z$  303 for F8426-PAC,  $m/z$  326 for F8426-CI-PAC, and  $m/z$  326 or 361 for F8426-CAC. Approximate retention times are 4.2-5.7, 4.8-6.5, 5.2-7.1, 5.2-7.3, and 5.3-7.5 minutes for F8426-BAC, F8426-PAC, F8426-CI-PAC, F8426-CAC, and carfentrazone-ethyl (F8426), respectively. In general, a confirmatory method was not used; on occasion multiple ions were monitored for F8426-CAC to confirm identification (p. 23).

ILV: The test compounds and loamy sand soil matrix were supplied by FMC Corporation (pp. 12-15 of MRID 49559801). The independent laboratory performed the extraction method as written, except 40 g samples of soil were fortified with the extraction solvent and procedural volumes adjusted accordingly (pp. 20-21). A 40-mL extract sample was taken for derivatization and the procedure then followed as written, except Agilent Bond Elut SI Silica (1 g/6 mL) SPE cartridges were used (pp. 16, 21). The 10x LOQ samples were diluted to 20% of original concentration using ethyl acetate. The following modifications to the GC/MS conditions were made: an Agilent 6890N GC system with Agilent 5973 MS, an Agilent HP-5 column (0.32 mm x 25 m, df = 0.52  $\mu$ m, injector temperature not specified), and injection volume of 1  $\mu$ L (pp. 16-17). The following ions were monitored:  $m/z$  330 for carfentrazone-ethyl (F8426),  $m/z$  335 for F8426-BAC,  $m/z$  303 for F8426-PAC,  $m/z$  326 for F8426-CI-PAC, and  $m/z$  361 for F8426-CAC (p. 18). Retention times were  $5.49 \pm 0.01$ ,  $6.29 \pm 0.01$ ,  $6.87 \pm 0.01$ ,  $7.00 \pm 0.01$ , and  $7.18 \pm 0.01$  minutes for F8426-BAC, F8426-PAC, F8426-CI-PAC, F8426-CAC, and carfentrazone-ethyl (F8426), respectively (p. 35).

LOQ and LOD: In the ECM and ILV, the LOQ and LOD for all analytes were 5  $\mu$ g/kg (ppb) and 1  $\mu$ g/kg, respectively (p. 12 of MRID 44165040; p. 27 of MRID 49559801).

## II. Recovery Findings

ECM (MRID 44165040): Procedural recoveries for soils from terrestrial field dissipation studies conducted in Finney County, Kansas (KS), and Polk County, Minnesota (MN), were reported to support validation of the ECM (p. 11; Tables 2-2f, pp. 28-34). Mean recoveries and relative standard deviations (RSDs) were within guidelines (mean 70-120%; RSD  $\leq$ 20%) for analysis of carfentrazone-ethyl (F8426) and its transformation products F8426-BAC, F8426-PAC, F8426-CI-PAC, and F8426-CAC in a sand soil (KS) and a silt loam soil (MN) at fortification levels of 5  $\mu$ g/kg (ppb, LOQ, n = 24-31), 10  $\mu$ g/kg (2x LOQ, n = 20-22), and 20  $\mu$ g/kg (2x LOQ, n = 6-14), with the following exceptions: 20  $\mu$ g/kg carfentrazone-ethyl (RSD 21%), 10  $\mu$ g/kg F8426-BAC (RSD 22%), and 20  $\mu$ g/kg F8426-CAC (RSD 30%) in the sand soil, and 5  $\mu$ g/kg carfentrazone-ethyl (RSD 23%), 10  $\mu$ g/kg F8426-CI-PAC (RSD 22%), and 5 and 10  $\mu$ g/kg F8426-CAC (RSD 21%) in the silt loam soil. At higher fortification levels of 40-100  $\mu$ g/kg (8x-20x LOQ) for the sand soil and 50-80  $\mu$ g/kg (10x-16x LOQ) for the silt loam soil, only one or two recoveries were reported for each fortification level; therefore, meaningful statistics (mean, standard deviation, RSD) for the recovery results per fortification level and soil matrix could not be generated. At the higher fortification levels, individual recovery results were within 70-120% with the following exceptions: 50  $\mu$ g/kg carfentrazone-ethyl (66%) in sand soil, and 70 and 80  $\mu$ g/kg carfentrazone-ethyl (66% and 68%, respectively), 70  $\mu$ g/kg F8426-BAC (65%), 50  $\mu$ g/kg F8426-PAC (62%), and 70  $\mu$ g/kg F8426-CI-

PAC (66%) in silt loam soil. In general, a confirmatory method was not used. The study author reported that on occasion multiple ions were monitored during repeat analyses of F8426-CAC to confirm the presence of the analyte (p. 23). Characterizations of the soil matrices were not provided.

**ILV (MRID 49559801):** Mean recoveries and relative standard deviations (RSDs) were within guidelines (mean 70-120%; RSD  $\leq$ 20%) for analysis of carfentrazone-ethyl (F8426), F8426-BAC, F8426-PAC, F8426-CI-PAC, and F8426-CAC in a loamy sand soil at fortification levels of 5  $\mu\text{g}/\text{kg}$  (LOQ) and 50  $\mu\text{g}/\text{kg}$  (10x LOQ; Table 12, p. 29). The method was validated for carfentrazone-ethyl, F8426-PAC, and F8426-CI-PAC at both fortification levels after one trial, and for F8426-BAC and F8426-CAC after two additional GC/MS analyses with the F8426-BAC 10x LOQ samples re-diluted from the original final sample extracts and monitoring F8426-CAC at  $m/z$  361 rather than  $m/z$  326 (p. 18). The F8426-BAC 10x LOQ samples were re-diluted because recoveries were slightly higher than acceptable levels in the first analytical run. The monitoring ion for F8426-CAC was changed to  $m/z$  361 because an interfering peak was detected at the retention time of F8426-CAC in the matrix control sample at  $m/z$  326 (Attachment I, Figure 7, p. 40). The first re-analysis of F8426-BAC and F8426-CAC was rejected because the run stopped prior to analyzing a bracketing standard at the end of the analysis (p. 18; Table 6, p. 24). The soil matrix, collected from Sycamore, Georgia, was supplied by FMC Corporation and characterized by Agvise Laboratories, Northwood, North Dakota (p. 15; Attachment II, Figure 15, p. 50). The method modifications and equipment substitutions implemented during the ILV (see **I. Principle of the Method, ILV:** above) are not considered substantial changes to the ECM.

**Table 2. Initial Validation Method Recoveries for Carfentrazone-ethyl (F8426) and its Transformation Products F8426-BAC, F8426-PAC, F8426-CI-PAC, and F8426-CAC in Soil<sup>1</sup>**

Analyte	Fortification Level ( $\mu\text{g}/\text{kg}$ )	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
<b>Sand Soil</b>						
Carfentrazone-ethyl (F8426)	5 (LOQ)	24	80-134	105	15	14
	10	20	60-149	103	19	19
	20	14	61-138	93	19	<b>21</b>
	40	<b>1</b>	92	-- <sup>2</sup>	--	--
	50	<b>1</b>	<b>66</b>	--	--	--
	100	<b>1</b>	91	--	--	--
F4826-benzoic acid (F8426-BAC)	5 (LOQ)	25	60-112	87	15	17
	10	20	44-109	85	18	<b>22</b>
	20	13	55-96	80	12	15
	40	<b>2</b>	88, 104	96	11	12
	50	<b>1</b>	93	--	--	--
	100	<b>1</b>	92	--	--	--
F8426-propionic acid (F8426-PAC)	5 (LOQ)	25	59-113	90	15	17
	10	20	61-117	96	14	14
	20	13	57-100	83	13	16
	40	<b>2</b>	97, 109	103	8	8
	50	<b>1</b>	93	--	--	--
	100	<b>1</b>	82	--	--	--

Analyte	Fortification Level (µg/kg)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
F8426-chloropropionic acid (F8426-Cl-PAc)	5 (LOQ)	24	80-125	103	13	13
	10	20	73-125	100	14	14
	20	12	71-120	98	12	13
	40	<b>1</b>	114	--	--	--
	50	<b>1</b>	88	--	--	--
	100	<b>1</b>	105	--	--	--
F8426-cinnamic acid (F8426-CAc)	5 (LOQ)	25	63-124	98	16	16
	10	22	61-125	98	15	16
	20	19	34-141	88	26	<b>30</b>
	50	<b>2</b>	90, 102	96	8	9
	100	<b>1</b>	89	--	--	--
<b>Silt Loam Soil</b>						
Carfentrazone-ethyl (F8426)	5 (LOQ)	31	57-142	89	20	<b>23</b>
	10	20	60-118	84	16	19
	20	6	72-98	82	10	12
	50	<b>2</b>	83, 88	86	4	4
	70	<b>1</b>	<b>66</b>	--	--	--
	80	<b>1</b>	<b>68</b>	--	--	--
F4826-benzoic acid (F8426-BAc)	5 (LOQ)	31	56-120	87	15	17
	10	20	53-107	82	15	19
	20	6	67-97	82	13	16
	50	<b>2</b>	65, 80	73	11	15
	70	<b>1</b>	<b>65</b>	--	--	--
	80	<b>1</b>	90	--	--	--
F8426-propionic acid (F8426-PAc)	5 (LOQ)	31	62-117	85	13	15
	10	22	63-127	92	18	19
	20	6	76-122	89	17	19
	50	<b>2</b>	62, 76	<b>69</b>	10	14
	70	<b>1</b>	77	--	--	--
	80	<b>1</b>	89	--	--	--
F8426-chloropropionic acid (F8426-Cl-PAc)	5 (LOQ)	31	75-142	107	16	15
	10	20	71-151	105	24	<b>22</b>
	20	6	78-120	98	15	15
	50	<b>2</b>	81, 82	82	1	1
	70	<b>1</b>	<b>66</b>	--	--	--
	80	<b>1</b>	75	--	--	--
F8426-cinnamic acid (F8426-CAc)	5 (LOQ)	31	46-133	88	18	<b>21</b>
	10	22	66-130	95	19	<b>21</b>
	20	11	64-98	79	10	12
	50	<b>1</b>	84	--	--	--
	70	<b>2</b>	71, 79	75	6	8
	80	<b>2</b>	84, 89	87	4	4

Data (recovery results, corrected when residues found in matrix controls; p. 25 of MRID 44165040) were obtained from Tables 2-2f, pp. 28-34 of MRID 44165040 and DER Attachment 2 (number of tests, means, SDs, and RSDs).

1 USDA classifications; however characterizations of soil matrices were not provided (p. 11 of MRID 44165040).

2 Not applicable, n = 1.

**Table 3. Independent Validation Method Recoveries for Carfentrazone-ethyl (F8426) and its Transformation Products F8426-BAc, F8426-PAc, F8426-CI-PAc, and F8426-CAC in Loamy Sand Soil<sup>1</sup>**

Analyte	Fortification Level (µg/kg)	Number of Tests	Recovery Range (%)	Mean Recovery (%)	Standard Deviation (%)	Relative Standard Deviation (%)
Carfentrazone-ethyl (F8426)	5 (LOQ)	5	87-123	108	14	13
	50	5	104-114	108	4	4
F4826-benzoic acid (F8426-BAc)	5 (LOQ)	5	88-110	101	9	9
	50	5	94-118	106	12	11
F8426-propionic acid (F8426-PAc)	5 (LOQ)	5	92-113	103	8	8
	50	5	106-121	113	7	6
F8426-chloropropionic acid (F8426-CI-PAc)	5 (LOQ)	5	77-122	102	17	16
	50	5	89-99	94	4	4
F8426-cinnamic acid (F8426-CAC)	5 (LOQ)	5	72-119	98	17	18
	50	5	94-135	111	15	13

Data were obtained from Table 12, p. 29 of MRID 49559801 and DER Attachment 2 (SDs).

<sup>1</sup> USDA classification (Attachment II, Figure 15, p. 50 of MRID 49559801).

### III. Method Characteristics

In the ECM and ILV, the LOQ for all analytes in soil was set at 5 µg/kg (ppb) and the LOD was estimated at 1 µg/kg (20% of LOQ), with no justification (pp. 12, 26 of MRID 44165040; p. 27 of MRID 49559801).

**Table 4. Method Characteristics for Carfentrazone-ethyl (F8426) and its Transformation Products F8426-BAc, F8426-PAc, F8426-CI-PAc, and F8426-CAC in Soil**

Parameter	Carfentrazone-ethyl (F8426)	F8426-benzoic acid (F8426-BAc)	F8426-propionic acid (F8426-PAc)	F8426-chloropropionic acid (F8426-CI-PAc)	F8426-cinnamic acid (F8426-CAC)		
Limit of Quantitation (LOQ)	5 µg/kg (ppb)						
Limit of Detection (LOD)	1 µg/kg (ppb)						
Linearity (calibration curve $r^2$ and concentration range)	ECM:	Not reported.					
	ILV:	$r^2 = 0.9957$	$r^2 = \mathbf{0.9944}$	$r^2 = 0.9963$	$r^2 = \mathbf{0.9941}$	$r^2 = \mathbf{0.9861}$	
	Range:	100-800 pg/µL (ng/mL)					
Repeatable	ECM:	Sand:	Yes at 5 and 10 µg/kg. No at 20 µg/kg.	Yes and 5 and 20 µg/kg. No at 10 µg/kg.	Yes at 5, 10, and 20 µg/kg.	Yes at 5, 10, and 20 µg/kg.	Yes at 5 and 10 µg/kg. No at 20 µg/kg.
		Silt loam:	Yes at 10 and 20 µg/kg. No at 5 µg/kg.	Yes at 5, 10, and 20 µg/kg.	Yes at 5, 10, and 20 µg/kg.	Yes at 5 and 20 µg/kg. No at 10 µg/kg.	Yes at 20 µg/kg. No at 5 and 10 µg/kg.
		Both soils:	Insufficient number of fortifications (n = 1 or 2) at 40-100 µg/kg (8x-20x LOQ).				
	ILV:	Yes at LOQ and 10x LOQ for all analytes in loamy sand soil.					
Reproducible	Yes for loamy sand soil. However, the registrant did not verify that the ILV was conducted with a soil of the most difficult analytical sample condition.						
Specific <sup>1</sup>	ECM:	Interferences were sporadically detected for carfentrazone-ethyl (up to 47% of LOQ) and F8426-CAC (up to 34% of LOQ) in matrix control samples (p. 23; Tables 3-4e, pp. 35-46 of MRID 44165040). For carfentrazone-ethyl, interferences were found to be lab-incurred contamination removed by rinsing glassware with 0.25N HCl (p. 23). For F8426-CAC, interferences detected at $m/z$ 326 were not detected at $m/z$ 361 (Appendix B, Figure 27, p. 100).					

	ILV:	For carfentrazone-ethyl, F8426-BAc, F8426-PAc, and F8426-Cl-PAc, no interferences were detected at analyte retention times (Attachment I, Figures 6-7, p. 40 of MRID 49559801). For F8426-CAC, an interference detected at $m/z$ 326 (Run 1) was not detected at $m/z$ 361 (Run 3).
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Data were obtained from pp. 12, 19, 23, 26; Tables 3-4e, pp. 35-46; Appendix B, Figures 12-15, pp. 85-88; Figures 22-23, pp. 95-96; Figure 27, p. 100 of MRID 44165040; pp. 27, 35; Tables 7-11, pp. 25-27; Table 12, p. 29; Attachment I, Figures 1-7, pp. 37-40 of MRID 49559801; and DER Attachment 2.

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

- 1 A confirmatory method is typically not required where GC/MS and LC/MS methods are used as the primary method. For the ECM a confirmatory method was not generally used, but the study author reported that on occasion multiple ions were monitored during repeat analyses of F8426-CAC to confirm the presence of the analyte (p. 23). For the ILV, a confirmatory method was not used.

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

1. The loamy sand soil (7% clay, 0.39% organic carbon) used in the ILV was supplied by FMC with no justification (p. 15; Attachment II, Figure 15, p. 50 of MRID 49559801). For the ECM validation, the soil matrices were from terrestrial field dissipation studies conducted in Finney County, Kansas (KS), and Polk County, Minnesota (MN, p. 11 of MRID 44165040). The "surface soil" matrices were classified as sand (KS) and silt loam (MN); however, soil from 0-90 cm, divided into 10-cm segments was used (Tables 2-4e, pp. 28-46 of MRID 44165040). Characterizations were not provided for the soils used in the ECM validation. The registrant did not verify that the independent laboratory was provided with a soil of the most difficult analytical sample condition to analyze to demonstrate how well the method performs.
2. For the ILV, the linearity of the F8426-BAc, F8426-Cl-PAc, and F8426-CAC standard curves was not satisfactory; coefficients of determination  $r^2$  were not  $\geq 0.995$ .
3. The determination of the LOQ and LOD were not based on scientifically acceptable procedures as defined in 40 CFR Part 136, Appendix B. The LOQ for all analytes in soil was set at 5  $\mu\text{g}/\text{kg}$  (ppb) and the LOD was estimated at 1  $\mu\text{g}/\text{kg}$  (20% of LOQ), with no justification (pp. 12, 26 of MRID 44165040; p. 27 of MRID 49559801). Detection limits should not be based on the arbitrarily selected lowest concentration in the spiked samples.
4. Any communication between the independent laboratory and the study sponsor was not reported. The ILV indicated that "all discussions pertaining to the analytical procedures prior to the method validation were recorded and kept in the study file" (p. 35).
5. The ILV did not report quantitative analyses of reagent blank and soil matrix blank samples, and did not specify if recovery results were corrected for any residues detected in the matrix blank samples (Tables 13-17, pp. 30-34 of MRID 49559801). Chromatograms of reagent blank and soil matrix blank samples indicate no residues were detected (Attachment I, Figures 6-7, p. 40).

For the ECM validation, sample recoveries were corrected when residues were found in the matrix controls (p. 25; Tables 2-2f, pp. 28-34 of MRID 44165040).

6. For the ECM, an insufficient number of samples ( $n = 1$  or  $2$ ) were spiked at the 40, 50 (10x LOQ), 70, 80, and 100  $\mu\text{g}/\text{kg}$  fortification levels (DER Attachment 2).

At 5 (LOQ), 10, and 20 µg/kg fortification levels, method recoveries did not always meet OCSPP Guideline 850.6100 criteria for precision and accuracy (mean recoveries for replicates at each spiking level between 70% and 120% and relative standard deviations (RSD) ≤20% at the stated LOQ and at higher concentrations as follows:

Sand soil: 20 µg/kg carfentrazone-ethyl (RSD 21%), 10 µg/kg F8426-BAc (RSD 22%), and 20 µg/kg F8426-CAc (RSD 30%; DER Attachment 2).

Silt loam soil: 5 µg/kg carfentrazone-ethyl (RSD 23%), 10 µg/kg F8426-CI-PAc (RSD 22%), 5 and 10 µg/kg F8426-CAc (RSD 21%).

7. The ECM measures five compounds simultaneously. For the ECM validation, recovery results for all five analytes from an individual sample were not always reported. Recovery results for some analytes in an individual sample may have been reported, but results of one or more analyte(s) from the same sample were "rejected due to interferences, unacceptable recovery or unacceptable standard" (Tables 2-2f, pp. 28-34 of MRID 44165040).

Also for the ECM validation, some fortified samples were analyzed only for F8426-CAc. Those recovery results may have been from reanalysis of samples monitored at *m/z* 361, instead of *m/z* 326, but the distinction was not clarified in the study report tables (p. 23; Tables 2-2f, pp. 28-34).

8. For the ECM, chromatograms of reagent blanks, chromatograms of sand soil matrix blank samples monitored for carfentrazone-ethyl, F8426-BAc, F8426-PAc, and F8426-CI-PAc, and chromatograms for spiked samples at the LOQ and 10× LOQ for all analytes in each matrix were not provided. Standard curve plots with coefficients of determination ( $r^2$ ) were not provided.
9. A confirmatory method was not used. However, the ECM study author reported that on occasion multiple ions were monitored during repeat analyses of F8426-CAc to confirm the presence of the analyte (p. 23 of MRID 44165040). Typically, a confirmatory method is not required where GC/MS and/or LC/MS methods are used as the primary method(s) to generate study data.
10. For the ECM validation, soil extracts in methylene chloride were stored at room temperature up to 9 months from the date of fortification and extraction to analysis (p. 12 of MRID 44165040).
11. For the ILV study report (MRID 49559801), the following typographical error was noted on page 13: "F8436-BAc" should read F8426-BAc.

The reviewer noted that the names for two of the metabolites, F8426-propionic acid (F8426-PAc) and F8426-chloropropionic acid (F8426-CI-PAc), were inconsistent between the ECM and ILV and within the ILV (Table 6, p. 71 of MRID 44165040; pp. 10, 12-14; Tables 9-10, p. 26 of MRID 49559801). In some places, the metabolites were named F8426-propionic acid and F8426-chloropropionic acid. The reviewer determined that the correct names for the metabolites were F8426-propionic acid and F8426-chloropropionic acid based on data from previously reviewed studies.



12. Time required for analysis was not specified in the ILV study report. It was reported for the ECM validation that a single analyst can prepare a set of nine samples in *ca.* 12 hours, followed by *ca.* 5 hours of GC/MS analysis (p. 23 of MRID 44165040). Preparation of the diazomethane solution requires an additional 5 hours.

## 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

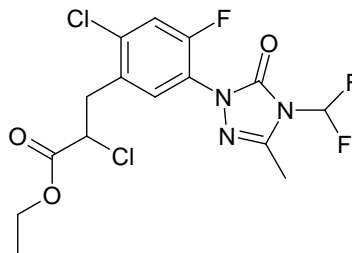
### Carfentrazone-ethyl (F8426, CR-50, FMC No. 116426)

**IUPAC Name:** Ethyl (RS)-2-chloro-3-{2-chloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorophenyl}propionate.  
Ethyl 2-chloro-3-(2-chloro-5-(4-difluoromethyl)-3-methyl-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl)-4-fluorophenyl)propanoate.

**CAS Name:** Ethyl  $\alpha$ ,2-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoate.

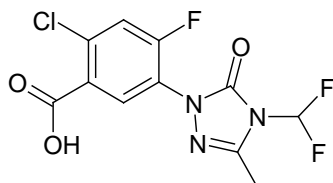
**CAS Number:** 128639-02-1

**SMILES String:** C1(CC(Cl)C(=O)OCC)C=C(N2C(=O)N(C(F)F)C(C)=N2)C(F)=CC=1Cl  
(EpiSuite version 4.0).

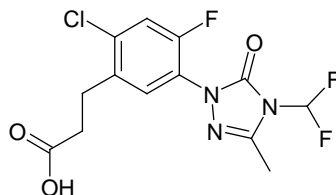


**F8426-benzoic acid (F8426-BAc, CR-11, FMC No. 97083)**

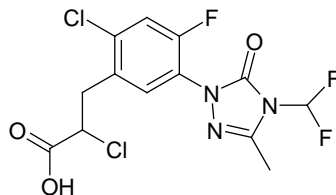
**IUPAC Name:** 2-Chloro-5-(4-(difluoromethyl)-3-methyl-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl)-4-fluorobenzoic acid.  
**CAS Name:** 2-Chloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1-H-1,2,4-triazol-1-yl]-4-fluorobenzoic acid.  
**CAS Number:** Not reported  
**SMILES String:** Not found

**F8426-propionic acid (F8426-PAc, FMC No. 125165)**

**IUPAC Name:** 3-(2-Chloro-5-(4-(difluoromethyl)-3-methyl-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl)-4-fluorophenyl)propanoic acid.  
**CAS Name:** 2-Chloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1-H-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoic acid.  
**CAS Number:** Not reported  
**SMILES String:** Not found

**F8426-chloropropionic acid (F8426-Cl-PAc, FMC No. 124161)**

**IUPAC Name:** 2-Chloro-3-(2-chloro-5-(4-difluoromethyl)-3-methyl-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl)-4-fluorophenyl)propanoic acid.  
**CAS Name:**  $\alpha$ ,2-Dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1-H-1,2,4-triazol-1-yl]-4-fluorobenzenepropanoic acid.  
**CAS Number:** 128621-72-7  
**SMILES String:** Not found



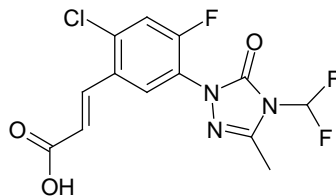
**F8426-cinnamic acid (F8426-CAc, FMC No. 125151)**

**IUPAC Name:** (Z)-3-(2-Chloro-5-(4-(difluoromethyl)-3-methyl-5-oxo-4,5-dihydro-1H-1,2,4-triazol-1-yl)-4-fluorophenyl)acrylic acid.

**CAS Name:** 2-Chloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1-H-1,2,4-triazol-1-yl]-4-fluorobenzenepropenoic acid.

**CAS Number:** 128639-10-1

**SMILES String:** Not found


**Attachment 2: Calculations**


128712\_44165040+\_  
DER-Fate\_850.6100\_

**Test Material:** Carfentrazone-ethyl  
**MRID:** 44165040  
**Title:** Analytical Methodology for The Determination of Carfentrazone-ethyl (F8426) and Its Metabolites in/on Bare Soil  
**MRID:** 49559801  
**Title:** Independent Laboratory Validation for the Determination of Carfentrazone-ethyl (F8426) and its Metabolites in Soil by GC-MS  
**EPA PC Code:** 128712  
**OCSPP Guideline:** 850.6100

**For CDM Smith**

**Primary Reviewer:** Lynne Binari  
**Signature:**   
**Date:** 5/19/15

**Secondary Reviewer:** Lisa Muto  
**Signature:**   
**Date:** 5/19/15

**QC/QA Manager:** Joan Gaidos  
**Signature:**   
**Date:** 5/19/15