

Fenpyrazamine; EPA PC Code 090109
Valent U.S.A. Corporation; EPA Company Code
ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT

Test Material: Fenpyrazamine

MRID 48400026
Title: Green, C.A. 2010. Independent laboratory validation of method RM-45S, *Determination of S-2188 and S-2188-DC in soil.*

MRID 48400026 - Appendix 2
Title: Kowalsky, J. 2008. Determination of S-2188 and S-2188-DC in soil, method RM-45S (Appendix 2, pp. 41, 50).

EPA PC Code: 090109

OCSPP Guideline: 835.6100

For Cambridge Environmental

Primary Reviewer: Lynne Binari

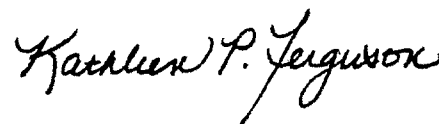
Signature:



Date: 2/14/12

Secondary Reviewer: Kathleen Ferguson

Signature:



Date: 2/14/12

QC/QA Manager: Joan Gaidos

Signature:



Date: 2/14/12

Fenpyrazamine; EPA PC Code 090109
Valent U.S.A. Corporation; EPA Company Code
ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT

Data Requirement: EPA Guideline: 835.6100
OECD Data Point: IIA 4.4

Test material:

Common name: Fenpyrazamine
Chemical name: 1H-Pyrazole-1-carbothioic acid, 5-amino-2,3-dihydro-2-(1-methylethyl)-4-(2-methylphenyl)-3-oxo-, S-2-propenyl ester (p. 21 of MRID 48399929).
IUPAC: Allyl 5-amino-2-isopropyl-4-(2-methylphenyl)-3-oxo-2,3-dihydro-1H-1-pyrazolecarbothioate

Primary Reviewer: Gabe Rothman, Environmental Scientist
U.S. EPA Office of Pesticide Programs, Environmental Fate and Effects Division

Date: 11/7/12

ANALYTICAL METHOD: EPA MRID No. 48400026 - Appendix 2. Kowalsky, J. 2008. Determination of S-2188 and S-2188-DC in soil, method RM-45S. Report prepared by Valent U.S.A. Corporation, Valent Technical Center, Dublin, California, sponsored and submitted by Valent U.S.A. Corporation, Walnut Creek, California; 14 pages. Final report issued July 7, 2008.

INDEPENDENT LABORATORY VALIDATION: EPA MRID No. 48400026. Green, C.A. 2010. Independent laboratory validation of method RM-45S, *Determination of S-2188 and S-2188-DC in soil*. Report prepared by Valent U.S.A. Corporation, Valent Technical Center, Dublin, California, sponsored and submitted by Valent U.S.A. Corporation, Walnut Creek, California; 90 pages. Final report issued October 6, 2010.

EXECUTIVE SUMMARY

This method is designed for the quantitative determination of residues of fenpyrazamine and S-2188-DC in soil using an external standardization method. The method was validated by Valent Technical Center; no regulatory guidelines were cited (Appendix 2, pp. 41-54). An "independent" laboratory validation (ILV), also performed by Valent Technical Center, was submitted with the method. *The Agency finds that this method meets the criteria for a scientifically valid method and is **acceptable** for (applicable residues).*

EPA MRID Number 48400026 (ECM/ILV)

Fenpyrazamine; EPA PC Code 090109

Valent U.S.A. Corporation; EPA Company Code

ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT

Method Summary: Analytes are extracted from soil by shaking with methanol:water (5:1, v:v), the extract is concentrated to the aqueous phase, cleaned up using solid phase extraction, and analytes are quantified by LC/MS/MS (Appendix 2, pp. 44-45). The ECM defined limits of quantitation (LOQ) and detection (LOD) of 0.02 mg/kg and 0.01 mg/kg, respectively, for both analytes, which were supported by the ILV (Appendix 2, p. 48, Appendix 5, pp. 89-90).

METHOD ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

The ILV was successful after one trial; however, it was not clearly defined that the personnel who performed the ILV were independent of those that validated the ECM. Also, two transition ions were monitored per analyte during LC/MS/MS analyses, indicating a confirmatory method was employed, however, supporting results from the confirmatory method were not provided.

Minor deficiencies of the ECM include an insufficient number of spiked samples at the LOQ. HPLC retention times for fenpyrazamine and S-2188-DE were not reported and chromatograms were illegible. Standard curve data used to generate reported residue results were not provided. Purities and lot numbers of analytes used were not reported. No characterization of the soil used for the fortifications. Preparation of soil prior to fortification was not described. Spiking procedures, including fortification solution used per spiking level and application solution volumes, were not described.

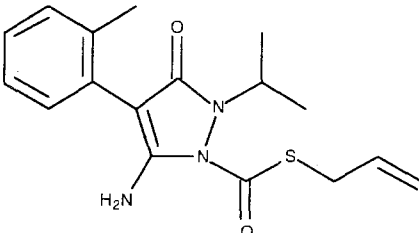
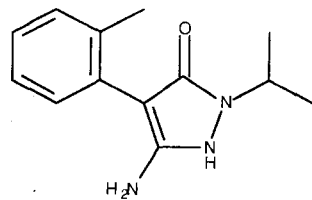
COMPLIANCE

No regulatory guidance was cited with the ECM (Appendix 2, pp. 41-54). The IVL was conducted in compliance with USEPA GLP Standards 40 CFR, Part 160 (p. 3). Signed and dated statements of No Data Confidentiality, GLP, Quality Assurance and Certificate of [report] Authenticity were provided with the ILV (pp. 2-3, 5-6).

A. BACKGROUND INFORMATION

Fenpyrazamine (S-2188) is a new fungicide being developed by Sumitomo Chemical for the control of gray mold and *Sclerotinia* rot in grape, oilseed rape and a variety of vegetables (p. 20 of MRID 48399929).

Fenpyrazamine; EPA PC Code 090109
 Valent U.S.A. Corporation; EPA Company Code
ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT

TABLE A.1. Test Compound Nomenclature	
Parameter	Value
Common name	Fenpyrazamine
Company experimental name	S-2188, V-10135
IUPAC name	Allyl 5-amino-2-isopropyl-4-(2-methylphenyl)-3-oxo-2,3-dihydro-1H-1-pyrazolecarbothioate
CAS Name	1H-Pyrazole-1-carbothioic acid, 5-amino-2,3-dihydro-2-(1-methylethyl)-4-(2-methylphenyl)-3-oxo-, S-2-propenyl ester
CAS #	473798-59-3
Structure	
Common name	S-2188-DC
Company experimental name	S-2188-DC
IUPAC name	Not reported.
CAS Name	Not reported.
CAS #	Not reported.
Chemical name	5-Amino-2,3-dihydro-2-(1-methylethyl)-4-(2-methylphenyl)-3-oxo-1H-pyrazole.
Structure	

Information obtained from pp. 12-13 of the study report (fenpyrazamine IUPAC and CAS names obtained from MRID 48399929, p. 21).

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound: Fenpyrazamine	
Parameter	Value
Physical state	Very pale yellow solid at 25°C
Odor	Characteristic of garlic
Melting point/range (°C)	116.4
pH	Not reported.
Relative Density at 20°C (g/mL)	1.250
Water solubility at 20°C (mg/L)	20.4 (OECD #105 - Flask Method)

EPA MRID Number 48400026 (ECM/ILV)

Fenpyrazamine; EPA PC Code 090109

Valent U.S.A. Corporation; EPA Company Code

ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound: Fenpyrazamine

Parameter	Value
Solvent solubility at 20 °C (g/L)	Hexane 0.811 Methylene dichloride >250 Acetone >250 Methanol >250
Vapor pressure at 20°C (Pa)	2.89×10^{-8}
Dissociation constant (pK _a)	No dissociation activity at pH 1-13
Octanol/water partition coefficient at 25°C (Log P _{ow})	3.52
UV/visible absorption spectrum at pH 7.8-8.1 (wavelength max, ε)	243 nm (16,700 M ⁻¹ cm ⁻¹) 274 nm (13,900 M ⁻¹ cm ⁻¹)

Information obtained from p. 24 of MRID 48399928.

B. MATERIALS AND METHODS

B.1. Principle of Method

Analytes are extracted from soil by shaking with methanol:water (5:1, v:v; Appendix 2, p. 44). The extract is concentrated to the aqueous phase which is loaded onto a SEP column (Waters Oasis HLB, 12 cc, 500 mg; Appendix 2, pp. 41, 44). Analytes are eluted with acetonitrile:water (1:1, v:v) and quantified by LC/MS/MS using a YMS ODS column, positive electrospray ionization (ESI⁺) and multiple reaction monitoring (MRM; Appendix 2, pp. 45-46). Two transition ions are monitored per analyte; 331.8 m/z > 229.9 and 188.9 m/z for fenpyrazamine, and 231.8 m/z > 189.5 and 145.2 m/z for S-2188-DC.

TABLE B.1. Summary Parameters for the Analytical Method Used for the Quantitation of Chemical Residues in Matrices Studied

Parameter	Value
Method ID	Determination of S-2188 and S-2188-DC in soil, method RM-45S (Appendix 2, p. 41).
Analyte(s)	Fenpyrazamine (S-2188) and S-2188-DC.
Extraction solvent/technique	1M sodium ascorbic acid (5 mL) is added to soil (10 g) and allowed to stand 10 minutes, then sample is extracted twice with methanol:water (5:1, v:v, 40 mL x 2) on reciprocating shaker for 1 hour per extraction (Appendix 2, p. 44).
Cleanup strategies	Extracts are filtered (Büchner funnel, Whatman #1 filter paper), combined and concentrated using rotary evaporation (<40°C) to remove methanol. The aqueous sample is loaded (gravity flow) onto a solid phase extraction column (Waters Oasis HLB, 12 cc, 500 mg) preconditioned with acetonitrile and water (Appendix 2, pp. 41, 44). The loaded column is rinsed with water (10 mL), followed by acetonitrile:water (1:10, v:v, 5 mL), then analytes are eluted with

TABLE B.1. Summary Parameters for the Analytical Method Used for the Quantitation of Chemical Residues in Matrices Studied

	acetonitrile:water (1:1, v:v, 25 mL). Dilute sample (250 µL) 1:4 with acetonitrile:water (1:1, v:v, 750 µL) for analysis.
Instrument/Detector	<u>ECM</u> - Hewlett Packard 1100 Quaternary HPLC system, with a YMC ODS column (3.0 x 100 mm, 3-µm), and Applied Biosystems API 2000 MS/MS triple quadrupole MS equipped with Turbo IonSpray ESI source in positive ionization mode (Appendix 2, pp. 43-46). <u>ILV</u> - Surveyor HPLC system, with a YMC ODS-AM column (3 x 100 mm, 3-µm), and Finnigan TSQ LC/MS/MS (ThermoElectron) triple quadrupole MS with positive mode electrospray ionization (pp. 13, 17).

Information obtained from pp. 13, 17, Appendix 2, pp. 41-46 of the study report.

C. RESULTS AND DISCUSSION

C.1. Recovery Results Summary

Analyte	Spiking Level (mg a.i./kg)	Mean Recoveries Obtained (%)	Relative Standard Deviation
Fenpyrazamine	0.02 (LOQ, n = 3)	87	2.3
	0.1 (n = 6)	87	2.9
S-2188-DC	0.02 (LOQ, n = 3)	88	2.8
	0.1 (n = 6)	100	4.7

Calculated by reviewer using results from Appendix 2, pp. 53-54 of the study report (DER Attachment 2).

C.1.1. Method Characteristics

Parameter	Value
Analyte(s)	Fenpyrazamine and S-2188-DC.
Limit of Quantitation (LOQ)	0.02 mg a.i./kg (Appendix 2, p. 48).
Limit of Detection (LOD)	0.01 mg a.i./kg (Appendix 2, p. 48)
Accuracy/Precision at LOQ	Acceptance criteria (EFED-ECM 2, Version 1, December 2010, p. 5) were met at the LOQ with matrix spike recoveries ranging between 70% to 120% and relative standard deviations of $\leq 20\%$ (Appendix 2, pp. 53-54, DER Attachment 2).
Reliability of the Method/[ILV]	The ILV was successful after one trial (p. 23, Table 1, p. 29).
Linearity	Nonlinear second-order polynomial regression - ECM r^2 = not reported; ILV r^2 = 0.9995-0.9999 (Appendix 5, pp. 89-90).
Specificity	Comparison of ILV chromatograms produced for standards and control and fortified samples demonstrates that the method, based on LC/MS/MS, is highly specific for the analysis of fenpyrazamine and S-2188-DC (Appendix 4, Figures 2-20, pp. 61-79, Figures 22-28, pp. 81-87). Any detections in reagent blank and matrix blank controls were $\leq 3\%$ of the LOQ (DER Attachment 2).

Information obtained from p. 23, Table 1, p. 29, Appendix 2, pp. 48, 53-54, Appendix 4, Figures 2-20, pp. 61-79, Figures 22-28, pp. 81-87, Appendix 5, pp. 89-90 of the study report and DER Attachment 2.

C.2. Independent Laboratory Validation (ILV)

Analyte	Spiking Level (mg a.i./kg)	Mean Recoveries Obtained (%)	Relative Standard Deviation
Fenpyrazamine	0.02 (LOQ)	90.9	6.5
	0.20	89.4	8.4
S-2188-DC	0.02 (LOQ)	85.9	7.0
	0.20	97.0	7.0

Results from Table 2, p. 30 of the study report.

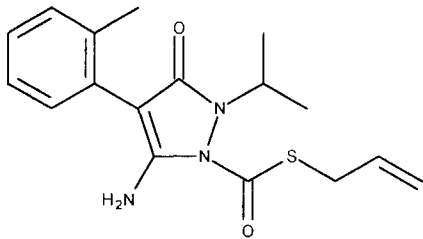
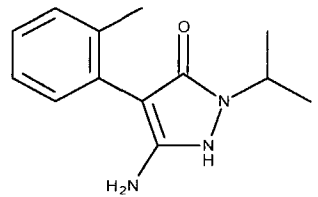
¹ Recoveries for fortified samples were corrected for mean residues detected in the control samples (p. 21, Appendix 5, pp. 89-90).

D. CONCLUSION

This method is designed for the quantitative determination of residues of fenpyrazamine and S-2188-DC in soil. *The Agency finds that this method meets the criteria for a scientifically valid method and is **acceptable** for (applicable residues).* Results from a confirmatory method were not provided. Also, it was not clearly defined that the personnel who performed the ILV were independent of those that validated the ECM.

Fenpyrazamine; EPA PC Code 090109
 Valent U.S.A. Corporation; EPA Company Code
ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT

DER ATTACHMENT 1. Fenpyrazamine and Its Environmental Transformation Products.^A

Code Name/ Synonym	Chemical Name	Chemical Structure	Study Type	MRID	Maximum % AR (day)	Final % AR (study length)
PARENT						
Fenpyrazamine S-2188	<p>IUPAC: S-allyl 5-amino-2,3-dihydro-2-isopropyl-3-oxo-4-(o-tolyl)pyrazole-1-carbothioate</p> <p>CAS: S-2-propen-1-yl 5-amino-2,3-dihydro-2-(1-methylethyl)-4-(2-methylphenyl)-3-oxo-1H-pyrazole-1-carbothioate</p> <p>CAS No.: 473798-59-3</p> <p>Formula: C₁₇H₂₁N₃O₂S</p> <p>MW: 331.4 g/mol</p> <p>SMILES: Cc1ccccc1c2c(n(n(c2=O)C(C)C)C(=O)SCC=C)N</p>		NG Method validation	48400026	NA	NA
S-2188-DC	<p>IUPAC: 5-Amino-2-isopropyl-4-(o-tolyl)-1H-pyrazol-3-one</p> <p>Formula: C₁₃H₁₇N₃O</p> <p>MW: 231.3 g/mol</p> <p>SMILES: Cc1ccccc1c2c([nH]n(c2=O)C(C)C)N</p>		NG Method validation	48400026	NA	NA
MAJOR (>10%) TRANSFORMATION PRODUCTS						
No major transformation products were identified.						

EPA MRID Number 48400026 (ECM/ILV)

Fenpyrazamine; EPA PC Code 090109
 Valent U.S.A. Corporation; EPA Company Code
ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT

Code Name/ Synonym	Chemical Name	Chemical Structure	Study Type	MRID	Maximum % AR (day)	Final % AR (study length)
MINOR (<10%) TRANSFORMATION PRODUCTS						
No minor transformation products were identified.						
REFERENCE COMPOUNDS NOT IDENTIFIED						
All compounds used as reference compounds were identified.						

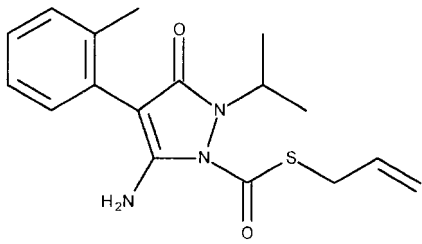
^A AR means "applied radioactivity". MW means "molecular weight".

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

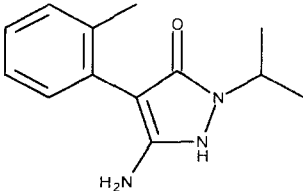
**ENVIRONMENTAL CHEMISTRY METHOD (ECM)
 STANDARD EVALUATION PROCEDURE (SEP) CHECKLIST:
 BACKGROUND AND INITIAL REVIEW INFORMATION**

Referenced page numbers appear in the uppermost right corner of each page of the MRID.

I. Background Information

A.	Title of Method	Determination of S-2188 and S-2188-DC in soil, method RM-45S (Appendix 2, p. 41).	
B.	ECM No.	[Leave blank. This is for BEAD ECB's use.]	
C.	MRID No.	48400026	
D.	Matrix	Soil	
E.	Analyte(s) detected	Compound:	
		Common name:	Fenpyrazamine
		IUPAC name:	Allyl 5-amino-2-isopropyl-4-(2-methylphenyl)-3-oxo-2,3-dihydro-1H-1-pyrazolecarbothioate
		CAS name:	1H-Pyrazole-1-carbothioic acid, 5-amino-2,3-dihydro-2-(1-methylethyl)-4-(2-methylphenyl)-3-oxo-, S-2-propenyl ester
		CAS No:	473798-59-3 (p. 12).
		Synonyms:	S-2188, V-10135. 2-Propenyl 5-amino-2-(1-methylethyl)-4-(2-methylphenyl)-3-oxo-2,3-dihydro-1H-1-pyrazolecarbothioate (Appendix 2, p. 42). S-2-Propen-1-yl-5-amino-2,3-dihydro-2-(1-methylethyl)-4-(2-methylphenyl)-3-oxo-1H-pyrazole-1-carbothioate (p. 12).
			

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

	Common name:	S-2188-DC
	IUPAC name:	Not reported.
	CAS name:	Not reported.
	CAS No:	Not reported.
	Synonyms:	5-Amino-2,3-dihydro-2-(1-methylethyl)-4-(2-methylphenyl)-3-oxo-1H-pyrazole (p. 13).
		

Information obtained from pp. 12-13, Appendix 2, pp. 41-42 of the study report (IUPAC and CAS names obtained from MRID 48399929, p. 21).

II. Information about the Laboratory

A.	Name	Valent Technical Center (p. 5, Appendix 2, p. 41).
B.	Address	6560 Trinity Court, Dublin, California 94568 (p. 5).
C.	Telephone No.	Not reported.
D.	Name of the Study Director	Not reported.
E.	Name of the Lead Chemist	Not reported; method written by J. Kowalsky (Appendix 2, p. 50).
F.	Laboratory Validation:	Not provided.

Information obtained from p. 5, Appendix 2, pp. 41, 50 of the study report.

III. Method Summary Information for Analyte(s): Fenpyrazamine (S-2188) and S-2188-DC

A.	Statement of Data Confidentiality	Yes (p. 2).
1.	Is the Method Classified or Confidential?	No.
2.	Submitted Prior to 2008 with a Non-Standard Claim of Confidentiality?	No.

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

B.	Sample Preparation	Soil (10 g) was fortified with a mixed solution of fenpyrazamine and S-2188-DC, in acetonitrile, at 0.02 and 0.1 mg a.i./kg (Appendix 2, pp. 43, 53-54). Application volumes were not reported.
C.	Sample Extraction	1M sodium ascorbic acid (5 mL) added to soil (10 g) and let stand 10 minutes; extract twice with methanol:water (5:1, v:v, 40 mL x 2) on reciprocating shaker for 1 hour per extraction (Appendix 2, p. 44).
D.	Sample Cleanup	Filter extracts (Büchner funnel, Whatman #1 filter paper), combine; remove methanol using rotary evaporation (<40°C); load (gravity flow) aqueous sample onto a solid phase extraction column (Waters Oasis HLB, 12 cc, 500 mg) preconditioned with acetonitrile and water (Appendix 2, pp. 41, 44). Loaded column rinsed with water (10 mL), followed by acetonitrile:water (1:10, v:v, 5 mL), then analytes eluted with acetonitrile:water (1:1, v:v, 25 mL). Dilute sample (250 µL) 1:4 with acetonitrile:water (1:1, v:v, 750 µL).
E.	Sample Derivatization (if applicable)	None reported.
F.	Sample Analysis	LC/MS/MS (Appendix 2, p. 41).
1.	Instrumentation	Hewlett Packard 1100 Quaternary HPLC system and Applied Biosystems API 2000 MS/MS triple quadrupole MS equipped with Turbo IonSpray ESI source in positive ionization mode (Appendix 2, pp. 43, 45-46).
2.	Primary Column	YMC ODS column (3.0 x 100 mm, 3-µm; Appendix 2, p. 45).
3.	Confirmatory Column (if any)	None reported.
4.	Detector	Multiple Reaction Monitoring (MRM; Appendix 2, p. 45).
5.	Other Confirmatory Techniques (if any)	Two ion transitions were monitored per analyte: 331.8 m/z > 229.9 and 188.9 m/z for fenpyrazamine and 231.8 m/z > 189.5 and 145.2 m/z for S-2188-DC (Appendix 2, pp. 45-46).

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

6.	Other Relevant Information	LC conditions: gradient mobile phase combining (A) 0.05% acetic acid in water and (B) acetonitrile [percent A:B at 0.0-2.0 min. 80:20 (v:v), 4.0-15.0 min. 20:80, 15.5-21.0 min. 80:20], column temperature 20 ± 1°C, injection volume 50 µL, flow rate 0.4 mL/minute (Appendix 2, p. 45). Retention times of fenpyrazamine and S-2188-DC were not reported in ECM; ILV reported times of <i>ca.</i> 6.8 and 4.6 minutes, respectively (p. 17).		
G.	Detection and Quantitation Limits			
1.	Limit of Quantitation (LOQ)			
	Claimed in Method	0.02 mg/kg (Appendix 2, p. 48).	Estimated	No. Validated by method.
2.	Limit of Detection (LOD)			
	Claimed in Method	0.01 mg/kg (Appendix 2, p. 48).	Estimated	Yes. Calculated by dividing lowest analyte concentration from validated linear standard range (0.001 µg/mL) by matrix concentration in sample extract (0.1 g/mL).
H.	Recovery (Accuracy)/Precision Data; expressed as percentage of applied¹			
	Spiking Level (mg a.i./kg)	Parameter	Fenpyrazamine	S-2188-DC
	0.02 (LOQ, n = 3)	Range	85-89	87-91
		Mean	87	88
		SD	2.0	2.5
		RSD	2.3	2.8
	0.1 (n = 6)	Range	83-90	94-109
		Mean	87	100
		SD	2.5	4.7
		RSD	2.9	4.7

Information obtained from pp. 2, 17, Appendix 2, pp. 41, 43-46, 48, 53-54 of the study report.

¹ Calculated by reviewer using results from Appendix 2, pp. 53-54 of the study report (DER Attachment 2).

IV. Detailed Information about the Method

	YES	NO	REVIEW FURTHER
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ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

		YES	NO	REVIEW FURTHER			
A.	Does the method require spiking with the analytes(s) of interest?	x		Appendix 2, p. 44.			
B.	If the method requires explosive or carcinogenic reagents, are proper precautions explained?			Not applicable.			
C.	Is the following information supplied?						
1.	Detailed stepwise description of:						
a.	The sample preparation procedure?					x	
b.	The sample spiking procedure?					x	
c.	The extraction procedure?				x		Appendix 2, p. 44.
d.	The derivatization procedure?						Not applicable.
e.	The clean-up procedure?				x		Appendix 2, p. 44.
f.	The analysis procedure?				x		Appendix 2, pp. 45-46.
2.	Procedures for:						
a.	Preparation of standards?				x		Appendix 2, pp. 43, 47.
b.	Calibration of instrument?	x		Appendix 2, p. 45.			
3.	List of glassware and chemicals	x		Appendix 2, pp. 41-44.			
a.	Are sources recommended?	x		Sources for most reagents and glassware, but all standard use items.			
b.	Are they commercially available?	x					
4.	Name, model, etc., of the instrument, column, detector, etc., used?	x		Appendix 2, pp. 43-44.			
a.	Are sources recommended?	x					
b.	Are they commercially available?	x					
5.	LOD						
a.	Is there an explanation of how it was calculated?	x		Appendix 2, p. 48.			

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

		YES	NO	REVIEW FURTHER
b.	Is it a scientifically accepted procedure?	x		
c.	Is the matrix blank free of interference(s) at the retention time, wavelength, etc., of the analyte(s) of interest?		x	Appendix 2, Figures 1-2, pp. 51-53.
6.	LOQ			
a.	Is there an explanation of how it was calculated?	x		Appendix 2, p. 48.
b.	Is it a scientifically accepted procedure?	x		
7.	Precision and accuracy data			
a.	Were there an adequate number of spiked samples analyzed?		x	Only three replicates at LOQ (Appendix 2, pp. 53-54).
b.	Are the mean recoveries between 70-120%?	x		DER Attachment 2.
c.	Are the RSDs of the replicates 20% or less at or above the LOQ?	x		
8.	Description and/or explanation of:			
a.	Areas where problems may be encountered?	x		See method "NOTES" (Appendix 2, pp. 48-49).
b.	Steps that are critical?	x		HPLC Grade water must be used. Each Oasis HLB lot must be checked for analyte recovery.
c.	Interferences that may be encountered?		x	
9.	Characterization of the Matrix(ces)?		x	

Information obtained from Appendix 2, pp. 41-49, Figures 1-2, pp. 51-52, pp. 53-54 of the study report and DER Attachment 2.

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

V. Representative Chromatograms

		YES	NO	REVIEW FURTHER
A.	Are there representative chromatograms for:			
1.	Analyte(s) in each matrix at the LOQ and 10 x LOQ?	LOQ (ECM, ILV) 10 x LOQ (ILV)		Appendix 2, Figures 1-2, pp. 51-52; Appendix 4, Figures 11-20, pp. 70-79.
2.	Method blanks?	ILV	ECM	Reagent blanks were analyzed with no significant levels of residues detected at the retention times of the analytes (Appendix 4, Figure 8, p. 67, Figure 23, p. 82; Appendix 5, pp. 89-90).
3.	Matrix blanks?	ECM, ILV		Appendix 2, Figures 1-2, pp. 51-52; Appendix 4, Figures 9-10, pp. 68-69, Figure 24, p. 83; Appendix 5, pp. 89-90).

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

4.	Standard curves?	ILV (Appendix 4, Figure 1, p. 60, Figure 21, p. 80).	ECM	Nonlinear, second-order polynomial regression. ECM provided one "example" standard curve, but did not specify for which analyte and/or if used to generate reported fortification results (Appendix 2, p. 47).
a.	Do the standard curves have acceptable linearity?	ILV	Not reported for ECM	$r^2 = 0.9995-0.9999$ (Appendix 5, pp. 89-90).
5.	Standards that can be used to recalculate some of the values for analyte(s) in the sample chromatograms?	ILV	EMC	Appendix 5, pp. 89-90.
B.	Can the responses of the analytes(s) in the chromatograms of the lowest spiking level be accurately measured?	x		

Information obtained from Appendix 2, Figures 1-2, pp. 51-52, Appendix 4, Figure 1, p. 60, Figures 8-21, pp. 67-80, Figures 23-24, pp. 82-83, Appendix 5, pp. 89-90 of the study report.

VI. Good Laboratory Practice (GLP) Standards

		YES	NO	REVIEW FURTHER
A.	Is there a statement of adherence to the FIFRA GLP standards?	ILV	ECM	p. 3.

Information obtained from p. 3 of the study report.

VII. Independent Lab Validation (ILV)

		YES	NO	REVIEW FURTHER
A.	Was an ILV performed?	x		

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

B.	Was the validation independent?		Undefined	ECM and ILV both performed by Valent Technical Center, Dublin, CA (p. 7, Appendix 2, p. 41).
C.	Did the ILV's precision/accuracy data meet the criteria established in OPPTS Guideline 850.7100?	x		Table 2, p. 30.
D.	Were recommendations of major or minor modifications to the method made by the independent lab performing the ILV? If major modifications were suggested, what were they?	x		Minor (pp. 18, 25-26).
E.	Recovery (Accuracy)/Precision Data; expressed as percentage of applied (n = 7)¹			
	Spiking Level (mg a.i./kg)	Parameter	Fenpyrazamine	S-2188-DC
	0.02 (LOQ)	Range	82.5-101.5	79.1-95.3
		Mean	90.9	85.9
		SD	5.9	6.0
		RSD	6.5	7.0
	0.20	Range	78.4-100.6	87.0-106.8
		Mean	89.4	97.0
		SD	7.5	6.8
RSD		8.4	7.0	

Information obtained from pp. 7, 18, 25-26, Table 2, p. 30, Appendix 2, p. 41 of the study report.

¹ Results from Table 2, p. 30 of the study report; verified by reviewer (DER Attachment 2).

VIII. Completeness

		YES	NO	REVIEW FURTHER
A.	Has enough information been supplied to do a proper review?	x		

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

		YES	NO	REVIEW FURTHER
B.	Has enough information been supplied to do a laboratory evaluation, if requested?			
C.	Are all steps in the method scientifically sound?	x		
D.	Is a confirmatory method or technique provided?		x	Two ion transitions were monitored per analyte; however, no confirmatory results were provided.
E.	Check the category below which best describes this ECM.			
1.	Satisfactory [Acceptable]	x		
2.	Major Deficiencies	x		See Section <i>IX</i> . No. 1 below.
3.	Minor Deficiencies	x		See Section <i>IX</i> . No. 2 below.

IX. Recommendations

- ECM major deficiencies:
 - The ECM and ILV were both performed by personnel of Valent Technical Center, Dublin, California, and there was no qualifying statement to distinguish that the lab personnel who performed the ILV were independent from the personnel that validated the ECM.
 - Although two transition ions were monitored per analyte during LC/MS/MS analyses, no confirmatory results were provided. This is also a deficiency of the ILV.
- ECM minor deficiencies:
 - Insufficient number of spiked samples at LOQ.
 - HPLC retention times for fenpyrazamine and S-2188-DE were not reported.
 - Standard curve data used to generate reported residue results were not provided.
 - Purities and lot numbers of analytes used were not reported.

Fenpyrazamine; EPA PC Code 090109
EPA MRID Number 48400026 (ECM/ILV)

ENVIRONMENTAL CHEMISTRY METHOD REVIEW CHECKLIST

- No characterization of the soil used for fortifications. This is also a deficiency of the ILV.
- Preparation of soil prior to fortification was not described.
- Spiking procedures, including fortification solution used per spiking level and application solution volumes, were not described.
- Chromatograms were illegible.

Name and Dated Signature of Primary Reviewer

Steve Matt 12/7/12

