



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

OFFICE OF PESTICIDE PROGRAMS  
ENVIRONMENTAL CHEMISTRY LABORATORY

Mail Code 7503ECB  
Stennis Space Center, MS 39529-6000  
(228) 688-3216

December 10, 2008

**MEMORANDUM**

SUBJECT: Thiencarbazone-methyl - ECM0233S1-S6 (Amended) DP # 340003

FROM: Joseph Ferrario, Branch Chief  
BEAD/Environmental Chemistry Laboratory

TO: Margaret Ervin, ECM Gatekeeper  
OPP/Environmental Fate and Effects Division  
Information and Support Branch (7507P)

The EFED/Environmental Fate and Effects Division has requested an Environmental Chemistry Method Review of a method for the determination of Thiencarbazone-methyl and its metabolites in soil/sediment using the method submitted by Bayer CropScience in accordance with the registration of the above mentioned analyte, MRID No. 470700-43. The method and independent laboratory validation data, (MRID No. 470700-44), were reviewed and the conclusions included in the attached Environmental Chemistry Method Review Report.

The following report includes an overview of the method and the method completeness, statements of adherence to EPA regulations, a presentation of results and a discussion of problems found in the registrant method and those discovered by the independent laboratory. A statement of method acceptability is also included.

If you have any questions concerning this report, please contact Elizabeth Flynt at (228) 688-2410 or me at (228) 688-3212.

Attachments

cc: Dr. Christian Byrne, QA Officer  
BEAD/Environmental Chemistry Laboratory

Elizabeth C. Flynt  
BEAD/ECL



2083200

Thiencarbazone-methyl in Soil/015804/Bayer CropScience/264  
**ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT**

**Data Requirement:** PMRA Data Code: NA  
EPA DP Barcode: 340003  
OECD Data Point: NA  
EPA Guideline: ECM Method Review

**Test material:**

**Common name:** Thiencarbazone-methyl  
**Chemical name:** Methyl 4-[[[(4,5-dihydro-3-methoxy-4-methyl-5-oxo-1H-1,2,4-triazol-1-yl)carbonyl]amino sulfonyl]-5-methyl-3-thiophenecarboxylate  
**IUPAC:** Methyl 4-[(4,5-dihydro-3-methoxy-4-methyl-5-oxo-1H-1,2,4-triazol-1-yl)carbonylsulfamoyl]-5-methylthiophene-3-carboxylate

**Primary Evaluator:** Elizabeth Flynt Date: 12/10/08  
Elizabeth Flynt, Chemist

**Peer Reviewer:** Shanda Bennett Date: 12/10/08  
Shanda Bennett, Chemist

**QA Officer:** Christian Byrne Date: 12/10/08  
Dr. Christian Byrne, QA Officer

**ANALYTICAL METHOD:** 470700-43, D. Netzband, J. Wade, March 14, 2007, "Analytical Method For The Determination of Residues of BYH 18636 And Its Metabolites BYH 18636-carboxylic acid, BYH 18636-sulfonamide, BYH 18636 sulfonamide-carboxylic acid, BYH 18636-MMT, and BYH 18636-triazolinone carboxamide in Soil and Sediment Using LC/MS/MS", The unpublished method was developed by Bayer CropScience of Stilwell, Kansas and sponsored by Bayer CropScience of Research Triangle Park, North Carolina. Pages 1 -55. The study no. is GS-003-S06-02. An independent laboratory validation was performed by Bayer CropScience AG of Monheim am Rhein, Germany, MRID No. 470700-44.

**EXECUTIVE SUMMARY**

The method is applicable for the quantitative determination of residues of Thiencarbazone-methyl and its metabolites in soil/sediment. The method was created by Bayer CropScience of Stilwell, Kansas in accordance with EPA's Good Laboratory Practice Standards, Title 40 Code of Federal Regulations Part 160. After a thorough review the ECB finds this method and its validation data acceptable.

**Method Summary**

Thiencarbazone-methyl and its metabolites are extracted from soil and sediment by adding 35:65 acetonitrile:deionized water and using microwave extraction. Following

Thiencarbazone-methyl in Soil/015804/Bayer CropScience/264  
**ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT**

the microwave extraction, isotopic internal standards are added to the extract, which is acidified and partitioned with ethyl acetate. The extract is then evaporated to dryness, reconstituted in 1:99 acetonitrile:water, and analyzed by LC/MS/MS.

The reported limit of quantification was found to be 2 ppb (ng/g) for Thiencarbazone-methyl (BYH 18636) and its metabolites.

**METHOD ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS**

This method is well documented and includes an ILV. The ILV initially reported several minor problems with the methods to the registrant which in turn made those corrections to the method before submitting it to EPA. This is the sequence that EPA encourages with regard to the role of the independent laboratory. The only minor problem discovered during the EPA review was an incorrect label on the X axis of the calibration curves.

This method appears acceptable for accurately determining Thiencarbazone-methyl residues and its metabolites in soil.

**COMPLIANCE**

Signed and dated statements that this method was conducted in accordance with the requirements for Good Laboratory Practice Standards, 40 CFR 160 were present in the method. Also present was a statement of non-confidentiality on the basis of the method falling within the scope of FIFRA Section 10 (d)(1)(A), (B), or (C).

**A. BACKGROUND INFORMATION**

Thiencarbazone-methyl is a triazolinone herbicide. Triazolinone herbicides are used in foliar and soil applications for treatment of annual broadleaf weeds.

<b>TABLE A.1. Test Compound Nomenclature</b>	
Compound	Chemical Structure <b>*See Appendix A for the chemical structure information</b>
Common name	Thiencarbazone-methyl
Company experimental name	BYH 18636
IUPAC name	Methyl-4-[(4,5-dihydro-3-methoxy-4-methyl-5-oxo-1 <i>H</i> -1,2,4-triazol-1-yl)carbonylsulfamoyl]-5-methylthiophene-3-carboxylic acid
CAS Name	Methyl 4-[(4,5-dihydro-3-methoxy-4-methyl-5-oxo-3- <i>H</i> -1,2,4-triazol-1-yl)carbonyl]sulfamoyl]-5-methyl-thiophene-3-carboxylate
CAS #	317815-83-1

Thiencarbazone-methyl in Soil/015804/Bayer CropScience/264  
**ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT**

<b>TABLE A.2. Physicochemical Properties of the Technical Grade Test Compound</b>	
Parameter	Value
Melting point/range	Not available
pH	Not available
Density	Not available
Water solubility (20 °C)	Not available
Solvent solubility (mg/ml at 20 °C)	Not available
Vapour pressure at ___ °C	Not available
Dissociation constant (pK <sub>a</sub> )	Not available
Octanol/water partition coefficient	Not available
UV/visible absorption spectrum	Not available

**MATERIALS AND METHODS**

**B.1. Principle of Method**

Thiencarbazone-methyl and its metabolites were extracted from soil and sediment by adding 35:65 acetonitrile:deionized water and using microwave extraction. Following the microwave extraction, isotopic internal standards are added to the extract, which is acidified and partitioned with ethyl acetate. The extract is then evaporated to dryness, reconstituted in 1:99 acetonitrile:water, and analyzed by LC/MS/MS.

<b>TABLE B.1.1.</b>	<b>Summary Parameters for the Analytical Method Used for the Quantitation of Chemical Residues in Matrices Studied</b>
Method ID	ECM0233S1-S6
Analyte(s)	BHY18636, BYH 18636-carboxylic acid, BYH 18636-sulfonamide, BYH 18636-MMT, BYH 18636-triazolinone carboxamide, BYH 18636-sulfonamide-carboxylic acid
Extraction solvent/technique	Microwave extraction using a 35:65 acetonitrile:water solution, followed by fortification with isotopic internal standard, centrifugation, and partitioning with ethyl acetate. The extract is evaporated to dryness, reconstituted in (1:99)(v:v) acetonitrile:water, filtered, and analyzed by LC/MS/MS.
Cleanup strategies	None
Instrument/Detector	Perkins Elmer Sciex API 4000 LC/MS/MS System equipped with a Turbo Ion Spray Source/Tandem Mass Spectrometry(MS/MS)

Thiencarbazone-methyl in Soil/015804/Bayer CropScience/264  
**ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT**

**C. RESULTS AND DISCUSSION**

**C.1. Recovery Results Summary**

**TABLE C.1.1. Recovery Results from Method Validation of Soil and Sediment**

*Soil*

Analyte	Spiking Level (ng/g)	Individual Recoveries	Mean Recovery ± SD (CV)
BYH 18636	2	96%, 95%, 98%, 97%, 95%, 95%, 95%, 100%, 100%, 97%, 98%, 98%, 99%, 98%	98 ± 1.8 (1.8)
	10	92%, 91%, 91%, 96%, 98%, 95%	94 ± 2.7 (2.9)
BYH 18636-carboxylic acid	2	79%, 78%, 79%, 80%, 79%, 82%, 79%, 84%, 81%, 81%, 82%, 80%, 85%, 82%	81 ± 2 (2.5)
	10	76%, 74%, 77%, 80%, 81%, 78%	77 ± 2.5 (3.3)
BYH 18636-MMT	2	89%, 89%, 93%, 88%, 87%, 90%, 91%, 89%, 97%, 102%, 101%, 97%, 98%, 93%	94 ± 5.1 (5.5)
	10	85%, 86%, 84%, 96%, 94%, 97%	90 ± 5.8 (6.5)
BYH 18636-sulfonamide	2	99%, 97%, 100%, 105%, 106%, 97%, 94%, 111%, 97%, 106%, 96%, 107%, 106%, 99%	101 ± 5.1 (5)
	10	100%, 93%, 90%, 99%, 91%, 101%	96 ± 4.8 (5)
BYH 18636-sulfonamide-carboxylic acid	2	92%, 88%, 86%, 88%, 89%, 84%, 86%, 83%, 82%, 83%, 82%, 84%, 83%, 84%	85 ± 2.6 (3.3)
	10	77%, 79%, 78%, 79%, 77%, 75%	78 ± 1.4 (1.7)
BYH 18636-triazolinone-carboxamide	2	101%, 103%, 99%, 100%, 98%, 101%, 102%, 97%, 97%, 91%, 90%, 92%, 92%, 99%	97 ± 4.4 (4.6)
	10	97%, 95%, 96%, 92%, 92%, 91%	94 ± 2.7 (2.8)

*Sediment*

Analyte	Spiking Level (ng/g)	Individual Recoveries	Mean Recovery ± SD (CV)
BYH 18636	2	99%, 99%, 99%, 100%, 100%, 99%, 102%	100 ± 1.1 (1.1)
	10	98%, 99%, 97%	98 ± 1 (1)
BYH 18636-carboxylic acid	2	83%, 84%, 82%, 82%, 82%, 82%, 84%	83 ± 1 (1.3)
	10	79%, 79%, 79%	79 ± 0.4 (0.5)
BYH 18636-MMT	2	97%, 89%, 91%, 86%, 87%, 88%, 90%	90 ± 3.7 (4.1)
	10	86%, 83%, 86%	85 ± 1.4 (1.7)
BYH 18636-sulfonamide	2	114%, 101%, 100%, 103%, 106%, 100%, 115%	106 ± 6.4 (6.1)
	10	103%, 101%, 116%	107 ± 8.5 (8)
BYH 18636-sulfonamide-carboxylic acid	2	78%, 76%, 80%, 77%, 79%, 77%, 82%	78 ± 2.2 (2.8)
	10	77%, 73%, 78%	76 ± 2.8 (3.7)
BYH 18636-triazolinone-carboxamide	2	103%, 102%, 104%, 106%, 102%, 103%, 106%	104 ± 1.8 (1.8)
	10	103%, 100%, 98%	100 ± 2.1 (2.1)

Thiencarbazone-methyl in Soil/015804/Bayer CropScience/264  
**ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT**

**C.1.2. Method Characteristics**

<b>TABLE C.1.2. Method Characteristics</b>	
Analyte	Thiencarbazone-methyl
Limit of Quantitation	2 ng/g
Limit of Detection (LOD)	0.1 to 0.3 ng/g (Soil); 0.1 to 0.4 ng/g (Sediment)
Accuracy/Precision at LOQ	See Table C.1.1.
Reliability of the Method/ [ILV]	An ILV was conducted successfully on this method
Linearity	Linear curves were prepared for each analyte. The correlation of coefficient for all ranged from $r = 0.9995$ to $0.9999$
Specificity	The method is very specific due to the use of MS-MS which is the most highly specific method for detection of residues at low conc.

**C.2. Independent Laboratory Validation (ILV)**

**TABLE C.2.1. Recovery Results Obtained by an Independent Laboratory Validation of the Method for the Determination of Thiencarbazone-methyl and its Metabolites in Soil-**

Analyte	Spiking Level (ng/g)	Mean recovery (%)	RSD (%)
BYH 18636	2	101	1.9
	20	97	1.3
BYH 18636-Carboxylic Acid	2	108	4.2
	20	102	4.8
BYH 18636-Sulfonamide	2	100	5.1
	20	97	2.6
BYH 18636-Sulfonamide-Carboxylic Acid	2	89	3.1
	20	97	3.3
BYH 18636-MMT	2	105	4.8
	20	103	2.2
BYH 18636-Triazolinone Carboxamide	2	85	5.3
	20	91	1.1

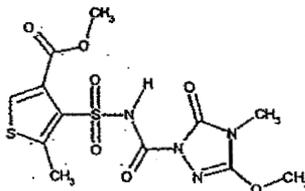
**D. CONCLUSION**

This is a well documented method which has been successfully validated by an independent laboratory. ECB finds the method acceptable as presented.

Thiencarbazone-methyl in Soil/015804/Bayer CropScience/264  
**ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT**

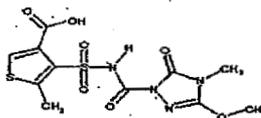
Appendix A: Thiencarbazone-methyl Chemical Structure

Code Name: BYH 18636 (AE 1162464)  
(Parent Molecule)



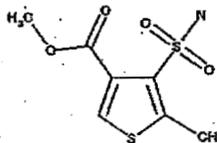
CAS Name: Methyl 4-[[[(4,5-dihydro-3-methoxy-4-methyl-5-oxo-1H-1,2,4-triazol-1-yl)carbonyl]amino]sulfonyl]-5-methyl-3-thiophenecarboxylate  
CAS Number: 317815-83-1  
Molecular Formula:  $C_{12}H_{14}N_4O_7S_2$   
Molecular Weight: 390  
ID No.: K-1439  
Reference No.: 0124200503  
Purity: 99.3%

Code Name: BYH 18636-carboxylic acid (AE 1394083)  
(Soil Metabolite)



CAS Name: 4-[[[(4,5-Dihydro-3-methoxy-4-methyl-5-oxo-1H-1,2,4-triazol-1-yl)carbonyl]amino]sulfonyl]-5-methyl-3-thiophenecarboxylic acid  
Molecular Formula:  $C_{11}H_{12}N_4O_7S_2$   
Molecular Weight: 376  
ID No.: K-1596  
Reference No.: 0203200604  
Purity: 99.2%

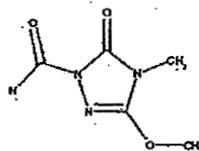
Code Name: BYH 18636-sulfonamide  
(Soil Metabolite)



CAS Name: Methyl 4-(aminosulfonyl)-5-methyl-3-thiophenecarboxylate  
CAS Number: 317815-81-9  
Molecular Formula:  $C_7H_9NO_4S_2$   
Molecular Weight: 235  
ID No.: K-1550  
Reference No.: 0210200501  
Purity: 99.3%

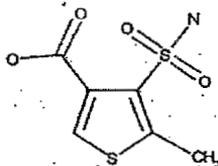
Thiencarbazone-methyl in Soil/015804/Bayer CropScience/264  
ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT

Code Name: BYH 18636-triazolinone carboxamide (AE 1430601)  
(Soil Metabolite)



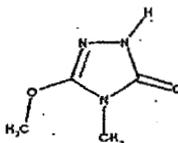
CAS Name: 4,5-Dihydro-3-methoxy-4-methyl-5-oxo-1H-1,2,4-triazole-1-carboxamide  
Molecular Formula: C<sub>5</sub>H<sub>8</sub>N<sub>4</sub>O<sub>3</sub>  
Molecular Weight: 172  
ID No.: K-1495  
E.R. Ref. No.: 0524200501

Code Name: BYH 18636-sulfonamide-carboxylic acid (AE 1395853)  
(Soil Metabolite)



CAS Name: 4-(Aminosulfonyl)-5-methyl-3-thiophenecarboxylic acid  
Molecular Formula: C<sub>6</sub>H<sub>7</sub>NO<sub>3</sub>S<sub>2</sub>  
Molecular Weight: 221  
ID No.: K-1380  
Ref. No.: 0615200405

Code Name: BYH 18636-MMT (AE 1277106)  
(Soil Metabolite)



CAS Name: 2,4-Dihydro-5-methoxy-4-methyl-3H-1,2,4-triazol-3-one  
CAS Number: 135302-13-5  
Molecular Formula: C<sub>4</sub>H<sub>7</sub>N<sub>3</sub>O<sub>2</sub>  
Molecular Weight: 129  
ID No.: K-1443  
E.R. Ref. No.: 95R-31-150A