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January 6, 2010

MEMORANDUM

EPA DP Barcode: 351881

SUBJECT: Oxamyl Studies in Soil (Revision No. 1)- Report No. ECM0243S1-S2

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

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

The Environmental Fate and Effect Division (EFED) has requested an Environmental Chemistry Method Secondary Review of a method (MRID No. 478659-01) for the determination of Oxamyl, and its metabolite Oxime in soil. The method was submitted by E. I. du Pont de Nemours and company in accordance with the registration of the above mentioned analytes. The method and independent laboratory validation data were reviewed and the conclusions included in the attached Environmental Chemistry Method Review Revision Attachment No. 1.

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. A statement of method acceptability is also included.

If you have questions concerning this report, please contact Charles Kennedy at (228) 688-2443 or Elizabeth Flynt at (228) 688-2410.

Attachments
cc: Christian Byrne, QA Officer
BEAD Environmental Chemistry Laboratory

Charles Kennedy
BEAD/Environmental Chemistry Laboratory

Oxamyl and Oxime in Soil/103801
E.I. du Pont de Neumours and Company/71654
ENVIRONMENTAL CHEMISTRY METHOD REVIEW REPORT
(Revision No. 1 Attachment)

Data Requirement: PMRA Data Code: NA
EPA DP Barcode: D351881
OECD Data Point: NA
EPA Guideline: ECM Method Review

Test material:
Common name: Oxamyl
CAS name: Methyl 2-(dimethylamino)-N-[[(methylamino)carbonyl]oxy-]-2-oxoethanimidothioate

Common name: Oxime metabolite
CAS: Methyl 2-(dimethylamino)-N-hydroxy-2-oxoethanimidothioate

Primary Evaluator: Charles Kennedy **Date:** 11/23/2009
Charles Kennedy, Chemist, EPA/OPP/BEAD/ECB

Peer Reviewer: Elizabeth Flynt **Date:** 12/16/09
Elizabeth Flynt, Chemist, EPA/OPP/BEAD/ECB

QA Officer: **Date:** 12/16/09
Dr. Christian Byrne, EPA/OPP/BEAD/ECB

ANALYTICAL METHOD: MRID No. 478659-01, Sergio C. Nanita, September 03, 2009, *Analytical Method for the Determination of Oxamyl and its Oxime Metabolite in Soil Using LC/MS Analysis (Revision No. 1)*. Unpublished method created by E. I. du Pont de Nemours and Company, DuPont Agricultural Products, Global Technology Division, Experimental Station, Wilmington, Delaware 19880-0402.

EXECUTIVE SUMMARY

This method is applicable for the overall quantitative determination of residues for oxamyl, and its metabolite oxime in soil. The method was submitted to EPA by E. I. du Pont de Nemours and Company of Wilmington, Delaware to support studies performed to seek registration for oxamyl and oxime in soil. It was also independently validated by E.I. du Pont de Nemours and Company of Wilmington, Delaware in accordance with U.S. EPA FIFRA (40 CFR Part 160) Principles of Good Laboratory Practice. The independent laboratory validation that was submitted with this method was entitled, *"Independent Laboratory Validation of Method Number DuPont – 2392, Analytical*

Method for the Determination of Oxamyl and its Oxime Metabolite in Soil Using LC/MS Analysis".

Method Summary: The analytical method involved the extraction of Oxamyl and its metabolite Oxime from soil using an accelerated solvent extractor (ASE) system. A subsample aliquot from this total extract volume was concentrated under nitrogen on a water bath and then diluted to a final extract volume. This final extract volume was then syringe filtered and analyzed using LC/MS.

The analytical method was sufficient to establish a limit of detection (LOD) and limit of quantitation (LOQ) for each analyte at 1.0 ppb and 10 ppb, respectively.

METHOD ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

A statement was presented that the U.S. EPA FIFRA (40 CFR Part 160) Good Laboratory Practice Standards were not applicable to analytical methods development. The method development work presented in this method was not done under GLP. However, analytical procedures, documentation, and archiving of the validation data were done following Standard Operating Procedures.

The original file names for the calibration standards at 10 and 20 ng/mL did not match the file names on the tables in Appendix 2 (Figures 4-9, Revision No. 1).

The tables in Appendix 2 for the LC/MS Raw Data Summary Sheet – SOIL Set 4318-97-OX-56 (LOQ and Method Validation Set #2) for Oxamyl and Oxime listed file names JUN14TD 014-1401 for 10 ng/mL and JUN14TD 016-1601 for 20 ng/mL. The original file name for the representative MS chromatogram of the 10 ng/mL oxamyl and oxime calibration standard is MSD1 TIC, MS File (JUN14TD\013-1301.D). A corrected file name (01-1401) was added above the file name. This correction was not accompanied by a line-out, initials and date as is standard practice in quality assurance.

The original file name for the representative MS chromatogram of the 20 ng/mL Oxamyl and Oxime calibration standard is MSD1 TIC, MS File (JUN14TD\015-1501.D. A corrected file name (016-1601) was added above the name. Again this correction was not accompanied by a line-out, initials and date. There is no file name that corresponds to the original file number in the tables of Appendix 2. There is an inconsistency in file numbering; the first file for standard 0.13 ng/mL is 002-0201 and continues through 016-1601 with 015-1501 missing. File 015-1501 is listed on Figure 9 as the file number for the standard 20 ng/mL.

Although evaluation of the method indicates that the linear regression calculations are acceptable, the information on the file name on the tables will continue to be incorrect. To address these deficiencies, it would be necessary for the registrant to make appropriate changes to the tables to reflect the original file name and not correct chromatograms with hand-written annotations. These issues notwithstanding, we were able to locate the pertinent information required to evaluate the method.

Under the conditions and parameters set in the Ecological Effects Test Guidelines, OPPTS 850.7100, Data Reporting for Environmental Chemistry Methods; "Public Draft." (U.S. Environmental Protection Agency Office of Prevention, Pesticides, and Toxic Substances (7101). U.S. Government Printing Office: Washington, DC, 1996, EPA-712-C-96-348), ECB finds this method acceptable for Oxamyl and its metabolite Oxime in soil.

COMPLIANCE

A signed and dated statement that the method was conducted in accordance with U.S. EPA FIFRA (40 CFR Part 160) Good Laboratory Practice Standards was not in the method. 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) was present.

A. BACKGROUND INFORMATION

Oxamyl is the active ingredient in the insecticide/nematicide Vydate® L used to control insects, mites, and nematodes in various crops while Oxamyl Oxime (Oxime) is its primary environmental metabolite.

TABLE A.1. Test Compounds Nomenclature

Compound	Chemical Structure *(See Appendix A for chemical structure information)
Common name	**Oxamyl**
Company name	**Oxamyl**
IUPAC Name	**(EZ)-N,N-dimethyl-2-methylcarbamoyloxyimino-2-(methylthio)acetamide**
CAS Name	**Methyl 2-(dimethylamino)-N-[[(methylamino)carbonyl]oxy-]-2-oxoethanimidothioate**
CAS Number	**23135-22-0**

TABLE A.2. Physicochemical Properties of the Technical Grade Test Compounds	
Parameter	Values
Melting Point/range	**100 - 102°C/White crystalline solid, at which point it changes to a different crystalline structure that melts at 108-110°C**
pH	**Not available**
Density	**Not available**
Water Solubility	**280 g/L @ 25°C**
Solvent solubility (20°C)	**Acetone - 14.5 g/L, Benzene - 1.4 g/L, Hexane - 0.8 g/L, Methanol – 21.5 g/L, and Xylene – 0.4 g/L**
Vapor Pressure	**31 mPa @ 25°C**
Dissociation constant (pK_a)	**Not available**
Octanol/water partition coefficient	**Not available**
UV/visible absorption sectrum	**Not available**

MATERIALS AND METHODS

B.1. Principle of Method

An analytical method was developed to quantify Oxamyl and its metabolite Oxime in soil. A soil sample of approximately 13 grams was extracted by acidified organic solvents at an elevated temperature and pressure using an Accelerated Solvent Extraction (ASE) 200 system. The samples were mixed with silica gel prior to loading into the ASE extraction cell.

A 5-ml aliquot of the total ASE extract volume was removed and a 1 ml aliquot of 0.01% aqueous formic acid was added. The extract was concentrated to approximately 1.5 ml under a nitrogen stream on a water bath at 40°C. The extract was then diluted to a final extract volume of 10 ml volume using a 0.01% aqueous formic acid solution. Further dilution may be necessary to approximate the residues expected in the soil extract so that it falls within the linear range of calibration standard concentrations used. The extracts were then mixed for 15-30 seconds and then sonicated for 1-2 minutes. The extract was then syringe filtered through a 0.2 µm Acrodisc® 13 PTFE disc and analyzed using LC/MS.

The fortification level for which recovery data were obtained was established as 10.0 ppb (LOQ) for Oxamyl and the metabolite Oxime. The method limit of detection (LOD) was determined to be at 1.0 ppb.

TABLE B.1.1.	**Summary Parameters for the Analytical Method Used for the Quantitation of Oxamyl and Oxime in Soil**
Method ID	ECM0243S1-S2
Analyte(s)	Oxamyl, Oxime
Extraction solvent/technique	Oxamyl and Oxime residues are extracted from soil into organic solvents using Accelerated Solvent Extraction (ASE®).
Cleanup strategies	Sample extracts were filtered using a syringes equipped with a 0.2 µm Acrodics ® 13 PTFE filter discs.
Instrument/Detector	Hewlett Packard Series 1100/API-ES/Single Stage Quadrapole Mass Selective Detector (MSD) using Single-Ion-Monitoring (SIM).

C. RESULTS AND DISCUSSION

C.1. Recovery Results Summary

Recovery Summary of Oxamyl In Soil

Sample Type	Fort. (ppb)	Mean	SD	RSD
Soil	10	96	7	7
Soil	30	90	2	3
Soil	100	93	9	11

Recovery Summary of Oxime In Soil

Sample Type	Fort.(ppb)	Mean	SD	RSD
Soil	10	90	6	7
Soil	30	90	2	2
Soil	100	95	8	10

C.1.2. Method Characteristics

TABLE C.1.2. Method Characteristics	
Analyte	Oxamyl and Oxime

C.1.2. Method Characteristics

TABLE C.1.2. Method Characteristics	
Analyte	Oxamyl and Oxime
Limit of Quantitation	10.0 ppb
Limit of Detection (LOD)	1.0 ppb
Accuracy/Precision at LOQ	See above chart
Reliability of the Method/ [ILV]	An independent laboratory validation [ILV], (MRID No. 455916-04), was conducted to verify the reliability of method (MRID No. 455916-03, 478659-01) for the determination of residues of Oxamyl and Oxime in soil.
Linearity	For the linear regression analyses, the coefficients of determination (r^2) were greater or equal to 0.9994 for all of the soil calibration curve determinations during the method validation.
Specificity	The method is specific for the determination of Oxamyl and Oxime by virtue of the chromatographic separation and selective detection system used.

C.2. Independent Laboratory Validation (ILV)

Method Validation Recovery Summary for Oxamyl and Oxime in Soil

Recovery Summary of Oxamyl in Soil

Type of Sample	Fort (ppb)	Mean	SD	RSD
Soil	10	90.6	5.98	6.6
Soil	100	104.6	5.02	4.8

Recovery Summary of Oxime in Soil

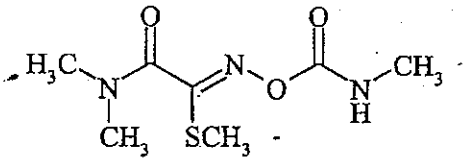
Type of Sample	Fort (ppb)	Mean	SD	RSD
Soil	10	99.8	1.92	1.9
Soil	100	89.2	4.21	4.7

D. CONCLUSION

From a review of the method, "*Analytical Method for the Determination of Oxamyl and its Oxime Metabolite in Soil Using LC/MS Analysis*"(Revision No.1), ECB concludes that the method is acceptable for determining the residues of Oxamyl and Oxime in soil for support of the registration studies.

Appendix A: Chemical Structure of Oxamyl and Oxime

Name or Code: Oxamyl
Chemical Name: Methyl 2-(dimethylamino)-N-[[(methylamino)carbonyl]oxy]-2-oxoethanimidothioate
CAS No: 23135-220
Monoisotopic Mass: 219.07



Name or Code: Oxime
Chemical Name: Methyl 2-(dimethylamino)-N-hydrox-2-oxoethanimidothioate
CAS No: 66344-33-0
Monoisotopic Mass: 162.05