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4-31-06

MEMORANDUM

SUBJECT: Clodinafop propargyl - ECM0219S1-S6
FROM: Joseph Ferrario, Branch Chief
BEAD/Environmental Chemistry Laboratory
TO: Hardip Singh
Senior Gatekeeper Team/IO EFED/
Environmental Risk Branch IV (7507C)

The EFED/Environmental Fate and Effects Division has requested an Environmental Chemistry Method Evaluation on Clodinafop propargyl in soil using the method submitted by Syngenta Crop Protection, Inc. in accordance with the registration of Clodinafop propargyl MRID No.460129-38. The method and independent laboratory validation data was reviewed and the conclusions included in the attached Environmental Chemistry Method Review Evaluation.

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

2052185

Clodinafop-propargyl/ECM0219S1-S6/125203/Syngenta Crop Protection/100
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Data Requirement: PMRA Data Code: NA
EPA DP Barcode: - D318319
OECD Data Point: NA
EPA Guideline: ECM Method Review

Test material:

Common name: Clodinafop
Chemical name: IUPAC: (R)-2-[4-(5-chloro-3-fluoro-2-yriddyloxy) phenoxy] propionic acid

Primary Evaluator: Elizabeth Flynt **Date:** 11/07/05
Elizabeth Flynt, Chemist, EPA/OPP/BEAD/ECB

Peer Reviewer: Charles Kennedy **Date:** 11/07/05
Charles Kennedy, Chemist, EPA/OPP/BEAD/ECB

QA Officer: Christian Byrne **Date:** 11/07/05
Dr. Christian Byrne, EPA/OPP/BEAD/ECB

ANALYTICAL METHOD: Chamkasem, Narong, 2002. Analytical Method 38-01 for the Determination of CGA-184927 and its Degradates CGA-193468, CGA-193469 and CGA-302371 and CGA-185072 (Safener) and its Degradate CGA-153433. Unpublished method created by Syngenta Crop Protection, Inc., 410 Swing Road, PO Bos 18300, Greensboro, NC 27419 and submitted by same. Study ID: Syngenta No. 38-01, Method Effective Date: April 19, 2002. Independent laboratory validation study completed on 2/21/2003.

EXECUTIVE SUMMARY

The method is applicable for the quantitative determination of residues of Clodinafop-Propargyl and 5 degradates in soil. The method was submitted to EPA to support studies performed to seek registration for Clodinafop-Propargyl. The method was created by Syngenta Crop Protection, Inc. in Greensboro, NC in accordance with EPA's Good Laboratory Practice Standards, Title 40 Code of Federal Regulations Part 160. An independent laboratory validation was submitted with this method. It was entitled, "Independent Laboratory Validation of Syngenta Report Number 38-01 for the Determination of Clodinafop-Propargyl (CGA-184927) and its Degradates CGA-193468, CGA-193469 and CGA-302371 and CGA-185072 (Safener) in Soil". It was performed by Syngenta lab at Jealott's Hill International Research Centre, Bracknell Berkshire, UK.

Method Summary: A soil sample (10 g) is extracted at room temperature with a mechanical shaker using 50/50% (v/v) acetone/buffer pH 7. The sample is centrifuged to obtain a clear supernatant and transferred into an aminopropyl (NH₂) SPE column (analytes are not retained). The eluate is collected in a beaker. The acetone is removed

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from the sample via rotary evaporation and brine and acetic acid are added to the sample. The sample is loaded into a Nexus Absolut SPE column with 1% formic acid/methanol and collected in a collecting flask. Methanol is evaporated and the aqueous sample is diluted with sample diluent and subsequently analyzed by LC/MS/MS.

The limit of quantification specified by the method which gives adequate recovery according to EPA guidelines is 0.5 ppb for all analytes in soil.

The precision/accuracy data obtained during the validation of the method was within the acceptable range of 70-120% recovery with a relative standard deviation less than 20% for the parent and all the degradates with the exception of CGA-153433. See Table C1.1. for details.

METHOD ACCEPTABILITY/DEFICIENCIES/CLARIFICATIONS

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), this method was acceptable for all analytes with the exception of CGA-153433. The recoveries for this analyte exceeded the prescribed range.

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, 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 signed and dated along with information on the Quality Assurance inspection dates and signatures.

A. BACKGROUND INFORMATION

Clodinafop-propargyl is a plant growth regulator. It is an oxyphenoxy acid ester herbicide used for the postemergent control of annual grasses in spring wheat.

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| Compound | R)-2-[4-[(5-chloro-3-fluoro-2-pyridinyl)oxy]phenoxy]propanoic acid |
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| | Chemical Structure |
| Common name | Clodinafop-propargyl |
| Company experimental name | CGA-184927 |
| IUPAC name | (R)-2-[4-(5-chloro-3-fluoro-2-pyridyloxy)phenoxy]propionic acid |
| CAS Name | (2R)-2-[4-[(5-chloro-3-fluoro-2-pyridinyl)oxy]phenoxy]propanoic acid |
| CAS # | 105512-06-9 |

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

| Parameter | Value |
|---|------------------------------------|
| Melting point/range | 48.2-57.1 C |
| pH | 4.1 @25C |
| Density | 1.37 g/cm ³ @22C |
| Water solubility (°C) | 4.0 ppm@ph7, 25C |
| Solvent solubility (mg/L at 20°C) | Not given |
| Vapour pressure at °C | 2.39 x 10 ⁻⁸ Pa at 25°C |
| Dissociation constant (pK _a) | |
| Octanol/water partition coefficient Log(K _{ow}) | Log P _{ow} = 3.90@25C |
| UV/visible absorption spectrum | |

B. MATERIALS AND METHODS

B.1. Principle of Method

| TABLE B.1.1. | Summary Parameters for the Analytical Method Used for the Quantitation of Chemical Residues in Matrices Studied |
|------------------------------|--|
| Method ID | ECM0219S1-S6 |
| Analyte(s) | Clodinafop-propargyl |
| Extraction solvent/technique | Liq/Liq extraction of soil with acetone/buffer pH7. The sample is centrifuged, decanted and evaporated, then reconstituted in brine and acetic acid. |
| Cleanup strategies | Nexus Absolut SPE column |

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| TABLE B.1.1. | Summary Parameters for the Analytical Method Used for the Quantitation of Chemical Residues in Matrices Studied |
| Instrument/Detector | LC/MS/MS - Waters 2690 HPLC coupled with a Micromass Quattro Ultima |

C. RESULTS AND DISCUSSION

| C.1. Recovery Results Summary Matrix | Spiking Level (ppb) | Average Recoveries Obtained (%) | Relative Standard Deviation |
|---|----------------------------|--|------------------------------------|
| Soil CGA-302371 | 0.5 | 82 | 7.9 |
| | 5.0 | 86 | 9.5 |
| CGA-153433 | 0.5 | 101 | 8.2 |
| | 5.0 | 134 | 24.3 |
| CGA-193468 | 0.5 | 73 | 7.0 |
| | 5.0 | 85 | 4.9 |
| CGA-193469 | 0.5 | 87 | 11.8 |
| | 5.0 | 93 | 12.9 |
| CGA-184927 | 0.5 | 74 | 9.7 |
| | 5.0 | 79 | 5.0 |
| CGA-185072 | 0.5 | 73 | 7.7 |
| | 5.0 | 75 | 2.9 |

C.1.2. Method Characteristics

| TABLE C.1.2. Method Characteristics | |
|--|--|
| Analyte | Clodinafop propargyl |
| Limit of Quantitation | 0.5 ppb |
| Limit of Detection (LOD) | 0.25 ppb |
| Accuracy/Precision at LOQ (0.5 ppb) | See chart above |
| Reliability of the Method/ [ILV] | An independent laboratory method validation [ILV], (MRID No. 460129-03), was conducted to verify the reliability of method (MRID No. 460129-38) for the determination of clodinafop propargyl residues and its degradates in soil. The values obtained indicated that the registrant method is acceptable according to <i>OPPTS 850.7100 Guidelines</i> with the exception of CGA-153433 which was not successfully validated by the registrant. |

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| | all compounds was greater than $r^2=0.9700$) |
| Specificity | The method is specific for the determination of chlodinafop propargyl and its degradates by virtue of the chromatographic separation and selective detection system used. According to recently published guidelines , when detection is performed by tandem mass spectrometry methods, confirmation of the presence of the analyte should require the observation of a precursor ion plus one structurally significant product ion observed at the same retention time. Further confirmation is not necessary due to the highly specific nature of the MS/MS transitions monitored. |

C.2. Independent Laboratory Validation (ILV)

The ILV was conducted in accordance with the *OPPTS 850.7100 Guidelines*. No method modifications were made.

| Matrix | Spiking Level (ug/g) | Average Recoveries Obtained (%) | Relative Standard Deviation |
|------------|----------------------|---------------------------------|-----------------------------|
| Soil | | | |
| | CGA-184927 | 0.5 ppb 5.0 ppb | 81 83 |
| CGA-193468 | 0.5 ppb 5.0 ppb | 85 82 | 7.1 3.1 |
| | CGA-193469 | 0.5 ppb 5.0 ppb | 91 88 |
| CGA-302371 | 0.5 ppb 5.0 ppb | 82 91 | 2.5 10.8 |
| | CGA-185072 | 0.5 ppb 5.0 ppb | 78 77 |

D. CONCLUSION

From a review of the method, Chamkasem, Narong, "Analytical Method 38-01 for the Determination of CGA-184927 and its Degradates CGA-193468, CGA-193469, CGA-302371 and CGA-185072 (Safener) and its Degradate CGA-153433 in Soil by High Performance Liquid Chromatography with Mass Spectrometric Detection", ECB concludes that the method appears scientifically sound and capable of determining the residues of Clodinafop and its degradates with the exception of CGA-153433 in soil at the limit of quantitation of 0.5 ppb and above.