PIB/FOD

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OCT 23 1990

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#09F3743 - Clethodim (Select®) in/on Soybeans, Cottonseed, and Animal Commodities. Reinitiation of Petition Method Validation Request (MRID No. 416234-01) [No DEB Number] (No Project Number)

FROM: Francis D. Griffith, Jr., Chemist
Chemistry Branch I - Tolerance Support
Health Effects Division (H7509C)

TO: Donald A. Marlow, Chief
Analytical Chemistry Branch
Biological and Economic Analysis Division (H7503C)

THRU: Richard D. Schmitt, Ph.D., Chief
Chemistry Branch I - Tolerance Support
Health Effects Division (H7509C)

Valent U.S.A. Corporation has proposed the establishment of revised tolerances for combined residues of the herbicide clethodim (ANSI), (E)-2-[1-(((3-chloro-2-propenyl)-oxy)imino)propyl]-5-[2-(ethylthio) propyl]-3-hydroxy-2-cyclohexen-1-one, and its metabolites containing the 2-cyclohexen-1-one moiety (calculated as the herbicide) in/on soybeans at 10 ppm; cottonseed at 1 ppm; meat, fat, and meat byproducts of cattle, goats, hogs, horses, poultry, and sheep at 0.2 ppm; milk at 0.05 ppm; eggs at 0.2 ppm, soybean soapstock at 15 ppm, and cottonseed meal at 2 ppm.

Clethodim is a NEW herbicide; there are no established tolerances. Clethodim is similar to sethoxydim (POAST Herbicide) in chemical structure, metabolic breakdown, proposed use, and proposed enforcement method (see sethoxydim in PAM II; 40 CFR 180.412).

A new petition method validation (PMV) is requested for three chemicals (parent clethodim and two metabolites) on soybeans, meat, and milk.

All samples (including controls) should be run in duplicate at the requested fortification levels (see attached table).

Two copies of the revised method (Valent Laboratory Project ID RM-26B-2, MRID No. 416234-01) along with supporting validation data (recoveries and sample chromatograms) are also attached. An earlier version of this method, i.e., RM-26A-1, has been validated by Craven Laboratories for cotton and soybean, by Analytical Development Corporation for meat and milk, and by EPL Bio-Analytical Services for poultry and eggs (see Attachment 3).

The extensively revised method, RM-26B-2, was prepared by Valent as a result of concerns noted in the E.S. Greer, ACB/BEAD memorandum of June 14, 1990 and M.J. Nelson, DEB/HED memorandum of June 20, 1990. These memoranda terminated the initial PMV request and remanded the method to the petitioner with the proviso that no new PMV would be initiated until suggested revisions were incorporated into the written procedure.

As the proposed primary enforcement method of the requested tolerances for clethodim, the petitioner has now submitted Analytical Method RM-26B-2, "The Determination of Clethodim Residues in Crops, Chicken and Beef Tissues, Milk, and Eggs, Method RM-26B-1," B. Ho, August 10, 1990, MRID No. 416234-01. RM-26B-2 supersedes previous versions (RM-26A-1 and RM-26A) of the basic method.

Method RM-26B-2 is a common moiety method, incapable of distinguishing between residues derived from clethodim and sethoxydim. The petitioner has submitted a confirmatory procedure (RM-26D-1) which is relatively specific for clethodim residues in the presence of sethoxydim residues. Since the initial DEB review by M.J. Nelson on March 12, 1990 noted that second laboratory validation data were required for the confirmatory procedure and none has been provided, no PMV will be requested at this time for the confirmatory method. When satisfactory second laboratory validation data are received for the confirmatory method RM-26D-1, then DEB plans to initiate a separate PMV request.

For right now, DEB requests that BEAD conduct a PMV trial of Analytical Method RM-26B-2. Two copies of RM-26B-2 (including representative chromatograms) are appended hereto (Attachment 2), along with information (Attachment 3) on recoveries via the predecessor versions of the method, and a summary of second laboratory validation results.

Please return the requested information on the attached Method Report Forms and all other information concerning the PMV that are generated according to your SOP on PMVs, including fortified samples, standard curves, and examples of sample calculations. A copy of any clethodim method supplied directly to ACB by Valent U.S.A. Corporation for this PMV should be returned to DEB with your final report.

Since a major reason for conducting a PMV is to assure that all necessary instructions are included in the method write-up, discussions of this PMV with Valent chemists and other Valent personnel should be discouraged until our evaluation is complete. This should not be construed as preventing contact with the company to clarify minor points. DEB does request that in your PMV report a summary of company contacts be provided to include the cause of the contact and what changes, if any, were made in the method. Again, for major problems encountered with the method, DEB requests the ACB chemist contact this reviewer (FDG) to ascertain whether or not to terminate the PMV. Any terminated PMV report should include a description of the problem(s) so that DEB can inform Valent of the problem(s) and request another revision of the method plus new validation data before initiating a new PMV request.

The parent clethodim standard is currently available from EPA's Pesticide and Industrial Chemicals Repository (telcon D. Griffith to P. Beyer, October 16, 1990). The Repository Code for clethodim is F-965. Three clethodim metabolites are also available from the Repository. They are clethodim sulfoxide (Repository Code F-959), 5-hydroxyclethodim sulfone (Repository Code F-961), and 5-methyl clethodim sulfoxide (Repository Code F-960).

However, the internal standard, cloproxydim sulfoxide, for use in the confirmatory method is not currently available from the Repository. The petitioner has been informed that this standard needs to be forwarded to the Repository and a 100 mg portion sent to the ACB lab in Beltsville (telcon D. Griffith to P. Pamidor of Valent, October 16, 1990).

Please obtain standards from EPA's Repository. When you have received both internal standards, they should be compared to determine if in fact the standards are the same. This will help ensure that Federal and State enforcement labs will receive the requested standards.

The review is not in expedite status. The Registration Division Product Manager for clethodim, Joanne Miller, should be contacted directly concerning the priority for completion of this PMV trial. The RD "projected return date" for this action is January 22, 1991.

Please address your written report to: Robert S. Quick, Section Head, Tolerance Petition Section I, Chemistry Branch - Tolerance Support, Health Effects Division (H7509C).

Attachments:

1) Method Report Form, 3 pages.

2) Two copies of the analytical method (R-M26B-1): "The Determination of Clethodim Residues in Crops, Chicken and Beef Tissues, Milk, and Eggs, Method RM-26B-2, B. Ho, August 15, 1990, 17 pages. MRID No. 416234-01.

3) Recovery information: Excerpt (pages 15 to 18) from DEB review of March 12, 1990, PP#9F3743.

cc: (With All Attachments):

P. Corneliussen (FDA, HFF-426)
R. Ellis (USDA, FSIS)

cc: (With Attachment 1 only):

Reviewer (FDG)
M. Bradley (DEB/PAM-II Co-Editor)
PP#9F3743
Reading File
Clethodim Subject File
Clethodim Registration Standard File
Circulation (7)

J. Miller (PM 23/RD)
C. Furlow (PIB/BEAD), Beltsville
H. Huntley (ACB/BEAD), Beltsville
R. Thompson (RTP-NC)

H7509C:DEB:Reviewer(FDG):CM#2:Rm814B:557-0826:JOB 55966:I:WP5.0:C.Disk:KENCO:10/18:90:de:vo:ek:de:ed:fdg:10/22/90.

RDI:SecHd:RSQuick:10/22/90:BrSrSci:RALoranger:10/22/90.

Attachment 1 Page 1 of 2

METHOD REPORT FORM

METHOD - Valent Analytical Method

"The Determination of Clethodim Residues in Crops, Chicken and Beef Tissues, Milk, and Eggs, Method RM-26B-2," B. Ho, August 15, 1990, 14 pages. MRID No. 416234-01.

Please do not use control values for recovery corrections.

Please do not report control values as 0.0 ppm. Accurately state your limit of detection and note any commodity coextractives that could change the recovery values reported. Also, please confirm the petitioner's claim for his limit of detection for parent clethodim and the two metabolites on the commodity listed below:

Commodity	Chemical Added*	ppm Added	ppm Found	% Recovery
Soybeans	C	0.0		
	"	0.5		
	"	5.0		
	5OH-SO_2	0.0		
	"	0.5		
	"	5.0		
Beef Liver	C	0.0		
	"	0.1		
	"	0.2		
	5OH-SO_2	0.0		
	"	0.05		
	"	0.1		
	SMSO	0.0		
	"	0.05		
	"	0.1		
Milk	C	0.0		
	"	0.02		
	"	0.04		
	5OH-SO_2	0.0		
	"	0.0125		
	"	0.025		
	SMSO	0.0		
	"	0.02		
	"	0.04		

*C = Clethodim; 5OH-SO_2 = 5-hydroxy clethodim sulfone; SMSO = S-methyl clethodim sulfoxide.

Modifications to Method (Major or Minor):

Special Precautions to be Taken:

Sources of Analytical Standards:

If derivatized standard used, give source.

Instruments for Confirmation:

If instrument parameters differ from method given, please list parameters used.

Commercial Source for any Special Chemicals or Apparatus:

Comments

Chromatograms