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

APR 19 1991

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

Subject: PP# 9F3743 - Clethodim (Select®) in/on Soybeans, Cottonseed, and Animal Commodities.
Evaluation of the Petition Method Validation Report on the Common Moiety Method.
(No MRID No.) [No DEB No.] (No HED Project No.)

From: Francis D. Griffith, Jr., Chemist
Chemistry Branch I - Tolerance Support
Health Effects Division (H-7509C)

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

To: Joanne I. Miller, Pm-23
Fungicide-Herbicide Branch
Registration Division (H7505C)

and

Donald A. Marlow, Chief
Analytical Chemistry Branch
Biological and Economic Analysis Division (H7503)

EXECUTIVE SUMMARY OF DEFICIENCIES

- Successful completion of Petition Method Validation (PMV) on proposed confirmatory or compound specific residue analytical method.

Chemistry Branch I - Tolerance Support (CBTS) has been informed by the Analytical Chemistry Section, Analytical Chemistry Branch (ACB) of the completion of the requested common moiety (primary) clethodim PMV. The results of PMV were reported by Douglas Swineford and Alex Krynitsky in their memorandum dated April 4, 1991.

1/4 15

The common moiety PMV was requested for clethodim (Select®) (E-2-[-1(((3-chloro-2-propenyl)-oxy)-imino)-propyl]-5-[2-ethyl thio)-propyl-3-hydroxy-2-cyclohexene-1-one) in soybeans, beef liver, and milk (see memorandum by F. D. Griffith, Jr. dated October 12, 1990, to ACB/BEAD). The common moiety PMV for clethodim and its metabolites in soybeans, beef liver, and milk was requested for the Valent Method RM-26B-2 dated August 15, 1990, and titled "The Determination of Clethodim Residues in Crops, Chicken and Beef Tissues, Milk and Eggs, Method RM-26B-2."

The PMV was conducted using the method as written by the petitioner, and as provided by CBTS. No modifications were made to the method by ACB. CBTS agrees with ACB that, based on review of the GC chromatograms of each commodity spiked with the various standards, we expect to see a detection limit of 0.05 ppm of parent clethodim or its metabolites in soybeans (10 gram sample), 0.025 ppm of clethodim and/or its metabolites in beef liver (25 gram sample), and 0.075 ppm of clethodim and/or its metabolites in milk (50 gram sample).

ACB notes that the molecular weights for clethodim and each of its metabolites were not included in the method write-up. The molecular weights should be included to determine the derivatization factors used to calculate recoveries. ACB has provided the molecular weights as received from Valent. CBTS agrees the molecular weights are a necessary part of the method and will recommend they be published in PAM-II as an EPA addendum to method RM-26B-2.

ACB also suggests that if chromatographic interferences were detected in various sample matrices, then the method users should try a longer mega bore column (i.e., 30 meters), or a 30 meter narrow bore column. Method users should also consider a different liquid phase such as DB-1701. CBTS agrees with these suggestions and will recommend these comments be published in PAM-II the same EPA addendum to method RM-26B-2.

CBTS requested the common moiety clethodim method be validated at 0.5 ppm and 5.0 ppm in soybeans for clethodim (as 3-[2-(ethylsulfonyl)propyl]pentanedionic acid dimethyl ester or DME) and 5-hydroxy clethodim sulfone (as 3-[2-(ethylsulfonyl)propyl]-3-hydroxypentanedioic acid dimethyl ester or DME-OH). The clethodim as DME recoveries from soybeans ranged from 73% to 86% (n = 4) and the 5-hydroxy clethodim sulfone as DME-OH recoveries ranged from 69% to 82% (n = 4).

In beef liver, CBTS requested the common moiety method RM-26B-2 be validated at 0.1 ppm and 0.2 ppm for clethodim (as DME) and at 0.05 ppm and 0.1 ppm for 5-hydroxy clethodim sulfone (as DME-OH) and S-methyl clethodim sulfoxide (as 3-[2-(methylsulfonyl)propyl]pentanedioic acid dimethyl ester or S-MeDME). Clethodim (as DME) recoveries from beef liver ranged

from 73% to 98% (n = 4), 5-hydroxy clethodim sulfone (as DME-OH) recoveries from beef liver ranged from 82% to 116% (n = 4), and S-methyl clethodim sulfoxide (as S-MeDME) recoveries ranges were 60% and 116% from the 0.05 ppm spike; and were 82% and 85% from the 0.1 ppm spike.

Clethodim and S-methyl clethodim sulfoxide fortifications in milk were 0.02 ppm and 0.04 ppm while the 5-hydroxy clethodim sulfone fortifications were 0.0125 ppm and 0.025 ppm. Using method RM-26B-2 clethodim (as DME) recoveries ranged from 81% to 109% (n = 4). 5-hydroxy clethodim sulfone recoveries from milk ranged from 103% to 127% (n=4). S-methyl clethodim sulfoxide recoveries from milk using method RM-26B-2 ranged from 81% to 107% (n = 4).

CBTS concludes from the above data that there has been a successful PMV for the clethodim common moiety method RM-26B-2. This method is suitable to gather total clethodim residue data in soybeans and cottonseed, and animal tissues. The method is tentatively suitable to enforce total clethodim tolerances that are proposed in this petition. To be an enforcement procedure for total clethodim tolerances this method must be used in conjunction with the compound specific method EPA-RM-26D-1. Method EPA-RM-26D-1 can separate clethodim and its metabolites from sethoxydim and its metabolites. A PMV has been requested for EPA-RM-26D-1. However, additional method validation data are needed from the petitioner before this PMV can be completed.

The analytical reference standards for method RM-26B-2 are available from EPA's Pesticide and Industrial Chemicals Repository at Research Triangle Park, North Carolina. The Repository codes are F-965 for clethodim, F-959 for clethodim sulfoxide, F-961 for 5-hydroxy clethodim sulfone, and F-960 for S-methyl clethodim sulfoxide.

ACB reports that two skilled analysts require 24 hours to prepare 6 samples for GC analysis plus use an additional 30 minutes for each GC sample injection. CBTS considers this time is marginally satisfactory for regulatory work.

CONCLUSION

DEB concludes that common moiety method RM-26B-2 as proposed for enforcement of total clethodim tolerances has had a successful PMV. The method is suitable to gather residue data and tentatively suitable to enforce proposed tolerances. To enforce the tolerances that are proposed in this petition Method RM-26B-2 (common moiety method) must be used with the compound specific method EPA-RM-26D-1 to identify and separate total clethodim from total sethoxydim. The petitioner needs to submit additional method validation data for EPA-RM-26D-1 before the PMV can be completed.

RECOMMENDATION

At this time CBTS recommends that the common moiety method RM-26B-2 for total clethodim residues not be forwarded to either FDA's Technical Editing Group for publication in PAM-II, or to PIB/FOD for distribution to interested parties. Once the compound specific method EPA-RM-26D-1 for clethodim residues has completed a successful PMV, CBTS could recommend for the requested tolerance, and then both methods will be forwarded for FDA and PIB/FOD.

cc: RF., Circ (7), Reviewer (FDG), PP#9F3743, R.F. Thompson (Repository-RTP,NC), Clethodim Subject File, TOX, FDA (Cornelinssen-HFF 426), M.Bradley (PAM-II Coeditor/MTO file), D. Hill (OCM-NEIC-Denver), H. Hundley (ACB-Beltsville), PIB/FOD(Furlow).

H-7509C:CBTS:Reviewer(FDG):CM#2:Rm 814B:557-0826:4/16/91:mj:fdg:4/17/91.

RDI:SecHd:RSQuick:4/17/91:BrSrSci:RALoranger:4/17/91.