C. Furbow

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

APR 16 1991

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#9F3743-Chlethodim (Select®) in/on Soybeans Cottonseed, and Animal Commodities. Review of Preliminary Reports on Compound Specific/Confirmatory Method Validation Request. (No MRID #) [No DEB #] (No HED Project #)

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

Francis D. Griffith

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

R. Loranger for RDS

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 (H7503C)

Chemistry Branch I-Tolerance Support (CBTS) has been informed by the Analytical Chemistry Section of the Analytical Chemistry Branch (ACB) of the completion of their pre-trial review of the requested clethodim compound specific/confirmatory petition method validation (PMV). ACB's pre-trial reports were completed by Harvey H. Hundley in his reports dated March 26, 1991, and March 22, 1991. The memorandum of March 26, 1991 is included as Attachment I to this CBTS review.

The PMV was requested to confirm residues of parent clethodim (E-2-[-1(((3-chloro-2 propenyl)-oxy)-imino)-propyl]-5-[2-(ethylthio) propyl]-3 hydroxy-2-cyclohexene-1-one) and its metabolites containing the 2-cyclohexene-1-one moiety in the presence of an equivalent amount of sethoxydim (2-[1-(ethoxyimino) butyl]-5-[2-(ethylthio) propyl]-3-hydroxy-2-cyclohexene-1-one) and its metabolites containing the 2-cyclohexene-1-one moiety in soybeans, liver, and milk (see

Attachment II, memorandum by F.D. Griffith, Jr., dated February 22, 1991). The compound specific/confirmatory PMV for clethodim and its metabolites on soybeans, liver, and milk was requested for the Valent Analytical Method EPA-RM-26D-1, dated December 14, 1990, and titled "Confirmatory Method for the Determination of Clethodim and Clethodim Metabolites in Crops, Animal Tissue, Milk, and Eggs."

Prior to starting the PMVs, ACB chemists normally review methods carefully, especially to see that reagents and equipment are adequately described, the method is adequately written with complete stepwise instructions, and sufficient and adequate validation data have been presented. During the ACB review of the PMV request, questions arose on the amount of validation data presented, including second laboratory validation data. The goal of this compound specific/confirmatory PMV was to be able to accurately confirm qualitatively and quantitatively clethodim and selected metabolites if sethoxydim and selected metabolites were also present. The parent compound clethodim and selected metabolites chosen for the compound specific PMV were the same and at the same fortification levels as in the common moiety method PMV (see memorandum of October 23, 1990 by F.D.Griffith Jr., which is included as Attached III). Discussions between ACB chemists and CBTS chemists centered on the point: was the validation data presented, including second laboratory validation data, adequate to proceed with the compound specific PMV, or would the fortifications requested for various compounds become method development. We concluded the fortifications chosen for the compound specific method did not have sufficient validation data from the petitioner; thus, the Agency would be doing method development. Agency policy has been and is that our labs validate existing data and do not do method development. The compound specific PMV will proceed for the metabolites and at levels for which adequate method validation data exists. The PMV can be completed once the petitioner provides the requested method validation data that is acceptable to the Agency.

The Agency needs to have adequate analytical enforcement methods for clethodim so that enforcement labs can separate clethodim from sethoxydim. CBTS points out that the established sethoxydim tolerances in 40 CFR §180.412 are 5 ppm on cottonseed and 2 ppm in eggs. The proposed clethodim tolerances are 1 ppm in cottonseed and 0.2 ppm in eggs. Thus, it is imperative for enforcement agencies to have a proven confirmatory procedure that can be qualitative and reasonably quantitative for determinations between sethoxydim and clethodim in eggs between 0.2 ppm and 2.0 ppm and in cottonseed between 1 ppm and 5 ppm. To put the problem in a difference perspective, if a regulatory chemist using method RM-26B-2 found 2 ppm in cottonseed or 0.4 ppm in eggs, then no regulatory action can be initiated without the valid confirmatory method such as method EPA-RM-26D-1, to separate sethoxydim from clethodim.

CB reiterates that the method validation data, including second lab validation previously presented are satisfactory for the compounds and levels that were tested. The problem is there are not enough data presented for the compound specific PMV to proceed to completion as requested.

The petitioner is expected to provide the requested additional performance and recovery data for method EPA-RM-26-D-1 as discussed in the EPA-Valent meeting of April 9, 1991. The petitioner is also expected to define an analytical limit of detection (as opposed to a limit of sensitivity or quantification) for EPA-RM-26D-1 in the matrices for the PMV. As a result of this meeting CBTS plans to initiate a modified PMV on the compound specific method once the additional method validation data are received, reviewed, and accepted. While the final metabolites selected for the amended PMV on method EPA-RM-26D-1 and their fortification levels will depend on the data presented by Valent it is our intent to modify the compound specific method PMV along the following lines as discussed in our April 9 meeting. Our request for validation data for sethoxydim and its metabolites for method EPA-RM-26D-1 is not to validate the method for enforcement of sethoxydim tolerances. Rather it is to prove that if sethoxydim and its metabolites were present in samples that contained clethodim and its metabolites, sethoxydim would not interfere with the identification and quantitation of clethodim.

For soybeans the petitioner is expected to provide clethodim sulfoxide/sulfone or clethodim, and 5-hydroxyclethodim sulfoxide/sulfone method validation data at 2 levels. While CBTS prefers 5.0 ppm and 0.5 ppm validation data to match proposed tolerances in cottonseed and soybeans and the levels in the common moiety method PMV, we will accept validation data at other levels that could validate the method at the proposed tolerances and at the level of detection or sensitivity. Also the petitioner is expected to provide method validation data at the same levels as in the clethodim soybean spikes for sethoxydim sulfoxide/sulfone or sethoxydim and 5-hydroxysethoxydim sulfoxide/sulfone;ie, the same analytical moiety.

After reconsideration of the results of the ruminant metabolism and feeding studies CBTS will no longer request petitioner or PMV validation data for 5-hydroxy clethodim sulfoxide/sulfone and the corresponding 5-hydroxy sethoxydim sulfoxide/sulfone; or for the S-methyl clethodim sulfoxide plus its corresponding sethoxydim analog in beef liver. The specific method PMV for beef liver will be modified to validate only clethodim sulfoxide/sulfone, or clethodim along with sethoxydim sulfoxide/sulfone, or sethoxydim at one level; ie, at or near the proposed secondary tolerance in meat byproducts(0.2 ppm).

Likewise in milk CBTS will no longer request petitioner or PMV validation data for 5-hydroxy clethodim sulfoxide/sulfone and

the corresponding 5-hydroxy sethoxydim sulfoxide/sulfone. The petitioner is expected to provide S-methyl clethodim sulfone with or without the corresponding sethoxydim metabolite method validation data at 2 levels. CBTS prefers recovery data at 0.02 ppm and 0.04 ppm to match the proposed tolerance and the levels used in the common moiety method. Method validation data that are at or near the proposed milk tolerance and near the limit of detection are acceptable. The petitioner is also expected to provide recovery data from milk for clethodim sulfoxide/sulfone and sethoxydim sulfoxide/sulfone at the same levels as for the S-methyl clethodim sulfoxide.

For the compound specific method quantitation of recoveries is necessary. However, the recoveries need not in all cases be 70% or greater. The Agency has the common moiety method that will give quantitation of clethodim and its metabolites that is adequate for enforcement purposes. It is intended that this method serve as a check on the results of the common moiety method.

In response to concerns noted in the ACB March 22, 1991 memo CBTS suggests steps taken to procure the appropriate HPLC columns (deficiency 1), obtain the internal standard or marker compound cloproxydim sulfoxide from the Repository (deficiency 2), and obtain all necessary reference analytical standards for compound specific or confirmatory PMV from appropriate sources (deficiency 3) all continue in order that the parts of the confirmatory PMV that have sufficient method validation can proceed. Concerns noted in deficiencies 4 and 5 on lack of enough validation data are discussed above in our request for the petitioner to provide additional method validation data. The portions of the PMV that can proceed will not be changed in our amended PMV.

CONCLUSIONS AND RECOMMENDATIONS

There are insufficient method validation data at present for the compound specific or confirmatory method PMV on EPA-RM-26D-1 to proceed as requested. Additional validation data as outlined and discussed above for clethodim and metabolites in the presence of sethoxydim and its metabolite are required for soybeans, liver, and milk.

The PM should forward this memorandum with its 3 attachments to the petitioner for action. Once CBTS has accepted these additional method validation data they will be forwarded to ACB so that the PMV can be completed.

The Analytical Chemistry Section of ACB should continue and complete that portion of the compound specific or confirmatory PMV on method EPA-RM-26D-1, for which adequate method validation data are on hand. The parts of the PMV that can proceed are as follows:

Soybeans

5-hydroxyclethodim sulfoxide for control, 0.5, and 5.0 ppm; 5-hydroxysethoxydim sulfoxide for control and 5.0 ppm.

Beef Liver

Sethoxydim sulfoxide (when available) for the control and 0.2 ppm. We note there will be no comparisons to other clethodim metabolites at this time.

Milk

Sethoxydim sulfoxide (when available) for the control and 0.05 ppm. We note there will be no comparisons to other clethodim metabolites at this time.

CBTS can not recommend for any clethodim tolerances until all PMVs have been successfully completed.

Attachment:

1) Memorandum by Harvey K Hundley dated March 26,1991, "Initiation of Petition Method Validation Request for Confirmatory Method," 2 pages,

2) Memorandum by F.D. Griffith, Jr., dated February 22,1991 "Initiation of Petition Method Validation request for Confirmatory Method," 7 pages,

3) Memorandum by F.D. Griffith, Jr., dated October 23,1990 "Reinitiation of Petition Method Validation Request," 6 pages.

H7509C:CBTS:Reviewer(FDG):vg:4/1/91:CM#2:RM814:557-7086:ed: fdg:4/8/91.

cc:R.F., Circu(7), Reviewer(FDG), PP#9F3743, R.D.Schmitt, Ph.D, Chief, H.K. Hundley (ACB/BEAD), C. Furlow (PIB/FOD), TOX, Clethodim Reg. Std. File, M. Bradley (CBTS, PAM-II Coeditor), R. Thompson (EPA-Repository, RTP-NC).

RDI:SecHd:RSQuick:4/12/91:BrSrSci:RALoranger:4/12/91.

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Attachment 1

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

Analytical Chemistry Section
Building 306, BARC-East
Beltsville, Maryland 20705

OFFICE OF
PESTICIDES AND TOXIC
SUBSTANCES

March 26, 1991

MEMORANDUM

SUBJECT: PP#9F3743 - Clethodim (Select) in/on Soybeans, Cottonseed, and Animal Commodities. Initiation of Petition Method Validation Request for Confirmatory Method. (MRID #417307-01) [No DEB No.] (No HED Request No.)

FROM: Harvey K. Hundley, Head
Analytical Chemistry Section

TO: Francis D. Griffith, Jr., Chemist
Chemistry Branch I - Tolerance Support
Health Effects Division/H7509C

In order for ACL to complete the requested validation study per your memo dated February 22, 1991, we need to be provided the following data information from the registrant at the fortifications levels requested.

1. Soybeans - Performance and recovery data for the parent chemicals - clethodim and sethoxydim and 5-hydroxysethoxydim sulfoxide at 0.5 ppm level.

2. Beef Liver - Performance and recovery data for the following:

   A. Clethodim parent
   B. Sethoxydim parent
   C. 5-hydroxyclethodim sulfoxide
   D. 5-hydroxysethoxydim sulfoxide
   E. S-methyl clethodim sulfoxide
   F. Sethoxydim sulfoxide for 0.05 and 0.1 ppm fortification levels. (Only data at 0.2 ppm was provided.)

3. Milk - Performance and recovery data for the following:

A. Clethodim parent
B. Sethoxydim parent
C. 5-hydroxyclethodim sulfoxide
D. 5-hydroxysethoxydim sulfoxide
E. S-methyl clethodim sulfoxide
F. Sethoxydim sulfoxide for 0.02 and 0.04 ppm fortification levels. (Only data at 0.05 ppm was provided.)

We shall proceed with the validation trial for 5-hydroxyclethodim sulfoxide and 5-hydroxysethoxydim sulfoxide on soybeans. It is important that we receive the remainder of registrant data as soon as possible in order to complete the laboratory validation as requested.

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Attachment C

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

FEB 22 1991

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: **PP#9F3743-Clethodim (Select®) in/on Soybeans, Cottonseed, and Animal Commodities. Initiation of Petition Method Validation Request for Confirmatory Method. (MRID#417307-01)[No DEB #](No HED Project #)**

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: Donald A. Marlow, Chief
Analytical Chemistry Branch
Biological and Economic Analysis Division (H-7503C)

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 (POST Herbicide) in chemical structure, metabolic breakdown, proposed use, and proposed enforcement method (see sethoxydim in PAM II; 40 CFR 180.412).

The proposed enforcement method, RM-26B-2 is currently undergoing a PMV (see memo of October 23, 1990 from F.D. Griffith, Jr. to D.A. Marlow). This petition method validation (PMV) request is new and for the proposed confirmatory method. The proposed enforcement method, RM-26B-2 is a common moiety method, incapable of distinguishing between residues derived from clethodim and sethoxydim. The petitioner has now submitted a

revised confirmatory procedure (RM-26D-1) which is relatively specific for clethodim residues in the presence of sethoxydim residues.

The extensively revised confirmatory method, RM-26D-1, was prepared by Valent as a result of concerns noted in the F.D. Griffith, Jr. memorandum of November 19, 1990 (Attachment II).

The petitioner has also submitted adequate second laboratory validation data. This work was performed by Analytical Development Corporation (ADC) of Colorado Springs, Co. These data have been reviewed by CBTS (see memo by F.D. Griffith., Jr. on December 13, 1990). The second lab validation data are in Attachment III to this request.

A new petition method validation (PMV) is requested for six chemicals (parent clethodim and sethoxydim plus 4 metabolites) on soybeans, meat, and milk for the confirmatory method.

The fortifications for the confirmatory method are at the same levels as for the clethodim enforcement method PMV. Two copies of the revised confirmatory method (Valent Laboratory Project ID EPA-RM-26D-1, MRID#417307-01) along with supporting validation data (recoveries, sample chromatogram and rational for used diazomethane as the methylating agent) are also presented as Attachment IV.

All samples (including controls) should be run in duplicate at the requested fortification levels (see Attachment I, Table).

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. CB-TS 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, CB-TS request 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 CB-TS 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). The internal standard cloproxydim sulfoxide (also known as

Selectone sulfoxide is available from the Repository as of December 13, 1991.

Please obtain standards from EPA's Repository. When you have received all standards, they should be compared to the registrants std. 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 data" for this action is July 20, 1991.

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.

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, 2 Pages.
2) Memorandum, PP#9F3743, F.D. Griffith, Jr., 11/19/90.
3) "Validation of Confirmatory Method for Determination of Clethodim Metabolites in Soybean Seed, Cotton Fuzzy Seed and Bovine Liver" J.F. Kruplak, October 31, 1990, 100 pages, File Accession #9012643. MRID#416850-01
4) Two copies of the Analytical Confirmatory Method (EPA-RM-26D-1) "Confirmatory Method for Determination of Clethodim and Clethodim Metabolites in Crops, Animal Tissues, Milk, and Eggs," J.C. Lai, December 14, 1990, 18 pages. MRID#417307-01.

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 Registration Standard File, Circulation (7), J. Miller (PM 23/RD)
C. Furlow (PIB/FOD), H. Huntley (ACB/BEAD), Beltsville
R. Thompson (RTP-NC).

H7509C:DEB:Reviewer(FDG):vg:CM#2:RM814B:557-0826:ed:fdg:2/22/91.
RDI:SecHd:RSQuick:2/20/91:BrSrSci:RALoranger:2/20/91.

ATTACHMENT 1

METHOD REPORT FORM

METHOD - Valent Analytical Method

"Confirmatory Method for the Determination of Clethodim and Clethodim Metabolites in Crops, Animal Tissues, Milk, and Eggs," Method RM-26D-1, J.C. Lai, December 14, 1990, 18 pages. MRID #417307-01

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	Chemicals Added*	Each Compound ppm Added	Individual ppm Found	Individual % Recovery
Soybeans	C + S	0.0		
	" "	0.5		
	" "	5.0		
	5OH-SO + S-5OH-SO	0.0		
	" "	0.5		
	" "	5.0		
Beef Liver	C + S	0.0		
	" "	0.1		
	" "	0.2		
	5OH-SO + S-5OH-SO	0.0		
	" "	0.05		
	" "	0.1		
	SMSO + SS	0.0		
	" "	0.05		
	" "	0.1		

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Milk	C + S	0.0
	" "	0.02
	" "	0.04
	5OH-SO + S-5OH-SO	0.0
	" "	0.0125
	" "	0.025
	SMSO + SS	0.0
	" "	0.02
	" "	0.04

*C = Clethodim; 5OH-SO_2 = 5-hydroxy clethodim sulfoxide SMSO = S-methyl clethodim sulfoxide; S = Sethoxydim; S5OH-SO_2 = 5-hydroxysethoxydim sulfoxide; SS = Sethoxydim 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

Attachment 2

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).

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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.

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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