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

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

APR 3 1996

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: 5F4440/5H5713: Pre-Trial Review of Analytical Methods for the Determination of Clethodim in Alfalfa, Dry Beans, and Peanuts

FROM: Everett Greer, Team Leader
Analytical Chemistry Section

THRU: Harvey Hundley, Head
Analytical Chemistry Section

THRU: Donald A. Marlow, Chief
Analytical Chemistry Branch

TO: José J. Morales, Chemist
Tolerance Petition Section II
Chemistry Branch I-Tolerance Support
Health Effects Division (7509C)

Reviewer's Introduction

The Analytical Chemistry Section pre-reviewed the following analytical methods submitted to EPA by Valent U.S.A. Corporation:

"Determination of Clethodim Residues in Alfalfa Commodities by the Confirmatory Method, EPA-RM-26D-2"

"Determination of Clethodim Residues in Dry bean Commodities by the Confirmatory Method, EPA-RM-26D-2"

"Determination of Clethodim Residues in Peanut Commodities by the Confirmatory Method, EPA-RM-26D-2"

The above methods are the study titles of three separate documents submitted to ACS for review. These documents range between 157 and 200 pages, and the actual method appears at about the middle of each document. The method itself, EPA-RM-26-D, has not been revised to include the analysis of alfalfa, bean and peanut commodities, but each document contains a section that describes modifications to the analytical procedure and critical steps that should be followed to accommodate the analysis of these matrices. Method EPA-RM-26D-2 should be revised to include these matrix specific modifications.

Alfalfa clethodim recoveries range between 45% and 124% for controls spiked at 5 ppm and lower, but recoveries at the "apparent" tolerance levels (10 ppm and 15 ppm for forage and hay respectively) are all above 70%. Recoveries below 5 ppm are somewhat erratic, and many of the values reported for clethodim sulfoxide and clethodim are below 70 %. LOQ's of 3 ppm for hay and 1 ppm for forage are reported. This method appears to be suitable for monitoring clethodim residues in alfalfa at the tolerance levels, but the analyst can expect poor recoveries and less reproducible results at lower levels. Control chromatograms show apparent analyte response to be much lower than response values at the "apparent" tolerances.

Dry bean recoveries were generally satisfactory, but high LOQ's were estimated for bean vines and hay. The highest LOQ values were half or less than the "projected" tolerances for these commodities. Control chromatograms displayed low apparent clethodim residue values in comparison to the analyte responses at the tolerance levels. The method seems satisfactory for monitoring clethodim residues in bean commodities at the tolerance levels, but reliable data probably cannot be expected at levels much lower then these for some of the analytes.

Peanut recoveries are somewhat erratic, but most of the very low results shown in Table I include analyses prior to using the modified silica elution wash. All recoveries using this modification were reported to be between 68 % and 108% for CSO, 63% and 93% for CS, and 48% and 96% for 5-OH CSO. The 48% recovery is for a hay sample spiked at 1.5 ppm with 5-OH CSO. Hay samples are reported to give a consistent 1 ppm interference for 5-OH CSO2. Therefor the petitioner states that this method is not reliable at residue levels below 2-3 ppm for this compound in hay. A 5 ppm tolerance level is proposed for peanut hay.

The petitioner states that "no interference peaks were found for CS/CSO and 5-OH CSO in untreated hull control samples", but the 200 mg equivalent chromatogram in Figure 2B-2 has numerous peaks around the retention time of the analytes. Chromatograms used to compare controls to fortifications near the tolerance levels do not give any significant interferences near the peaks of interest.

The method appears suitable for monitoring residues at the proposed tolerance levels for peanut commodities, but not enough data is provided, with the exception of the peanut hay samples, to evaluate the method at lower levels using the modified silica wash.

The method title states that this is a "confirmatory" procedure which would imply that the petitioner has previously submitted a primary enforcement method for these analyte/commodity combinations. If this is in fact correct, the method performance would be suitable for alfalfa, bean and peanut commodities. In any case the method appears to be acceptable, pending laboratory validation, for monitoring residues at the proposed tolerance levels. A problem would only potentially arise if this method were to be used for data collection at levels below the proposed tolerance limits.

Review of method EPA-RM-26-D

Extraction

Extraction volumes are given only for soybean seed and cotton fuzzy seed. Extraction volumes must be given for all commodities that the method is intended to be applied to.

Base Wash

The length of time needed to shake the separatory funnels should be stated.

Silica gel column

Silica column calibration should be described in detail.

Additional reviewer's comment

A justification for using diazomethane in the analysis is included with the method package.

Fred Kaus
6/7/96

Attachment:

INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL Clethodim

CODEX NO. 94

CODEX STATUS:

[ ] No Codex Proposal
Step 6 or Above

Residue (if Step 8): Sum of clethodim & metabolites containing 5-(2-ethylthiopropyl)cyclohexane-3-one and 5-(2-ethylthiopropyl)5-hydroxycyclohexane-3-one moieties and their sulphoxides and sulfones expressed as clethodim

Crop(s)	Limit (mg/kg)
beans, dry	0.1

PROPOSED U.S. TOLERANCES:

Petition No. 5F4440/5H57

DEB Reviewer J. Morales

Residue: Clethodim and its metabolites *

Crop(s)	Limit (mg/kg)
Alfalfa, forage	6
Alfalfa, hay	10
peanut, nutmeat	3
peanut, hay	3
peanut, meal	10
dry bean seeds	2

CANADIAN LIMITS:

[x] No Canadian Limit (on cited crops)

Residue: parent + moieties with 2-cyclohexyl-one moiety

Crop(s)	Limit (mg/kg)

MEXICAN LIMITS:

[x] No Mexican Limit (on cited c

Residue:

Crop(s)	Limit (mg/kg)

NOTES

* Contains the 5-(2-ethylthiopropyl) cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxy cyclohexene-3-one moieties and their sulfoxides and sulfones, expressed as clethodim