MEMORANDUM


FROM: G.F. Kramer Ph.D., Chemist
Tolerance Petition Section III
Chemistry Branch I, Tolerance Support
Health Effects Division (H7509C)

THRU: P.V. Errico, Section Head
Chemistry Branch I, Tolerance Support
Health Effects Division (H7509C)

TO: Carl Andreassen/Dennis Edwards (PM19)
Registration Division (H7505C)

CBTS requested that ACL in Beltsville conduct validation of an analytical enforcement method for chlorpyrifos in/on barley grain at 0.3 and 0.6 ppm and barley forage and straw at 1.5 and 3.0 ppm. The submitted analytical method (ACR 84.4.S3) was entitled: "Determination of Chlorpyrifos and 3,5,6-Trichloro-2-Pyridinol in Stone Fruit by Gas Chromatography - Modification for Chlorpyrifos in Lettuce, Snap Beans, Bell Peppers, Cucumbers, Grapefruit, and Sweet Corn," DowElanco, MRID# 428212-01. This Memo is an evaluation of the method validation performed by ACL (Memo, E. Hayes 9/10/93).

CONCLUSIONS/RECOMMENDATIONS

1. ACL made a major modification to the analytical method- a megabore column was substituted for the capillary or packed columns specified by the registrant. As a result of this substitution, the instrumental parameters (GC) were also changed.

2. The method was successfully validated using these revisions. The average recovery for barley grain was 90%; for barley forage, 102%; and for barley fodder, 92%.

3. The registrant must submit a revised copy of the enforcement method which incorporates the modifications made by ACL. The revised method will be submitted to FDA for inclusion in PAM II.

DETAILED CONSIDERATIONS

Validation

The method was performed as submitted with the exception of one modification- a megabore column was substituted for the capillary or packed columns specified by the registrant. ACL has found that better separations are achieved with the megabore column in applications of this type. As a result of this substitution, changes in the instrumental parameters (GC) were also necessitated.

No special precautions were necessary.

A set of 6 samples can be extracted, cleaned-up and chromatographed by one chemist in 8 hours.

The limit of detection was estimated to be 0.01 ppm.
Results

Barley RACs were fortified at or near the levels requested and analyzed with the revised method. The results are shown in Table 1. The values are the average of two separate determinations with the exception of barley grain fortified with 0.335 ppm which is the average of four determinations. This sample set was repeated due to poor recovery (54%) in one of the first two samples. With the exception of this grain sample, the recoveries ranged from 88-109%. This method meets the 40 CFR §158 and EPA's requirements as published in the Pesticide Assessment Guidelines, Subdivision O for Residue Chemistry (§171-4) as an enforcement method. However, the petitioner must revise the method as specified by ACL and submit a copy to the Agency. Complete details of the ACL modifications are found in the attachment.
Table 1- Recovery of chlorpyrifos from fortified barley RACs by method ACR 84.4.S3 as revised by ACL.

<table>
<thead>
<tr>
<th>RAC</th>
<th>ppm Added</th>
<th>Ave ppm Recovered</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barley Grain</td>
<td>0.000</td>
<td>0.000</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>0.335</td>
<td>0.295</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>0.603</td>
<td>0.562</td>
<td>93</td>
</tr>
<tr>
<td>Barley Forage</td>
<td>0.000</td>
<td>0.000</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1.500</td>
<td>1.613</td>
<td>108</td>
</tr>
<tr>
<td></td>
<td>3.000</td>
<td>2.856</td>
<td>95</td>
</tr>
<tr>
<td>Barley Straw</td>
<td>0.000</td>
<td>0.000</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1.500</td>
<td>1.440</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>3.000</td>
<td>2.682</td>
<td>89</td>
</tr>
</tbody>
</table>

Attachment: Memo from E. Hayes, ACS, ACL (9/10/93)

cc (without attachment): PP#3F4188/FAP#3H5662, S.F., Kramer, circ., R.F.
RDI: P.V. Errico (9/28/93), R.A. Loranger (9/28/93)
G.F. Kramer:804T:CM#2:(703)305-5079:H7509C
USER\CB:chlorpyr.8
Residue Chemistry Review

Comments:

Subject: Chlorpyrifos in/on Barley. Evaluation of Petition Method Validation.

Document

Class:
  Product
  Chem:
  Residue 860.1340 Residue analytical method
  Chem:

Biochemicals:

DP Barcode: D187788, D190700, D192629
MRIDs: 42821201

PC Codes: Actives 059101 Chlorpyrifos (ANSI)
Inerts

Commodities: Barley
Administrative #: 3F04188; 3H05662

Reviewers: G. F. Kramer

Approver: Philip V. Errico
Approved on: September 29, 1993

WP Document: Chlorpyr.0