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R.F.

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

DEC 18 1995

MEMORANDUM

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

Subject: **PP# 6F3392/FAP# 6H5500 - CLOFENTEZINE (APOLLO®) ON APPLES.** Evaluation of the Revised Tolerance Enforcement Method. (MRID #438008-01) [CBTS #s 16291 and 16292] {DP Barcode D219780 and D219782}

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and

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Biological and Economic Analysis Division (7503W)

Thru: Michael S. Metzger, Chief
Chemistry Branch I - Tolerance Support
Health Effects Division (7509C)

Michael S Metzger

INTRODUCTION

The petitioner submitted this amendment consisting of a cover letter dated September 26, 1995, signed by L.P. Czocher and a supplementary Section D (new residue analytical method) in response to deficiencies outlined and summarized in our March 23, 1995, review by F. Griffith (qv). Our conclusions and recommendation follow.

CONCLUSIONS

1. The petitioner has submitted a new/revised method, J-95R-02, for the Nor-Am method RAM J/02/92 to determine clofentezine residues in apples at 0.01 ppm.

2. The new method using, J-95R-02, uses a packed florisil cleanup column to improve clean-up of residues on apples at 0.01 ppm. CBTS concludes that the clean-up step has had a significant revision and now might be satisfactory to meet agency guidelines.

3. The petitioner did not, as suggested, extensively revise the method, RAM J/02/92, to incorporate the various ACB suggestions and to have the method meet all Agency Guidelines for an enforcement procedure.

4. ACB and CBTS concur that the new/revised clofentezine on apples at 0.01 ppm method, J-95R-02, will need an Agency tolerance method validation (TMV). The TMV is necessary to support the conclusion that the clean-up is satisfactory and to determine if all of our previous concerns have been addressed. The petitioner need not do a new ILV. The TMV will be initiated shortly.

RECOMMENDATION

CBTS reiterates its recommendation that the Nor-Am method RAM J/02/92 **NOT** be forwarded to FDA for publication as a generally acceptable residue analytical enforcement method for clofentezine on apples at 0.01 ppm. Method J-95R-02 should not be used by enforcement labs until it has been validated by EPA.

To allow time to evaluate the new/revised method, CBTS can support a continuation of the time limited tolerance of 0.01 ppm clofentezine on apples, if IRB/RD agree.

For purposes of continuing the time limited tolerance, CBTS has no objections to the new/revised method provided it is revised as suggested and can pass an EPA TMV, nor do we object to continued limited distribution of the method RAM J/02/92, to enforcement authorities provided the February and March 1995 Analytical Chemistry Branch (ACB) reports accompany the method to describe needed changes in the clean-up and determinative steps.

The following disclaimer must accompany method RAM J/02/92: "This method is for use only by experienced chemists who have demonstrated **knowledge** of the principles of trace organic analysis; and have proven **skills and abilities** to run a complex residue analytical method obtaining accurate results at the part per billion level."

DETAILED CONSIDERATIONS

The petitioner has submitted a new/revised method titled "Validation of an Analytical Method for Residues of Clofentezine in Fruit (Western Red Delicious Apples), USA, 1995" by J.L. Neal dated September 27, 1995 and coded laboratory ID J-95R-02 and **MRID # 438008-01.** With this submission the petitioner has elected not to revise method RAM J/02/92 as suggested in the CBTS memo dated March 23, 1995, by F. Griffith.

Method J-95R-02 used the same extraction, partitioning, concentration, and determination steps as were used in method RAM J/02/92. The difference was in the clean-up step. The new/revised method used a sample clean-up of 6 grams of activated florisil packed into a 25

cm X 10.5 mm id glass column with a 200 ml reservoir. Clofentezine is eluted off in 70 mls of ethyl acetate/hexane (15/85, v/v). The cleaned-up extract is rotary evaporated, then solvent exchanged to CH_3OH prior to HPLC analysis.

In the initial ACB screen and in the TMV reports several points were noted that would require clarification. CBTS reiterates the points are germane to the new/revised method. The petitioner will need to further revise the method and will need to include these comments in any method revision as additional instructions. We place particular emphasis on the standardization step in method RAM J/02/92 and suggest it be inserted into method J-95R-02. We also note that the petitioner has not identified the florisil or how to activate the florisil. Likewise, for method J-95R-02 CBTS suggests that the petitioner specify only anhydrous Na_2SO_4 be used and the source be identified. The specifications for the glass fiber filter paper used in method J-95R-02 need to be in the method write up as they were in method RAM J/02/92. The petitioner should not revise the method until ACB has completed its review of the method and the new TMV.

The petitioner validated the new/revised method at 0.01 and 0.1 ppm on raw apples only. Recoveries at 0.1 ppm ranged from 82 to 97%, n= 8. At the proposed tolerance level 3 recoveries were 56, 58, and 65% and when repeated they were 97, 100, and 105%. These data support our conclusion that the petitioner is proposing a LOD (limit of detection) method, not a LOQ (limit of quantitation) enforcement method. In the petitioner's hand the overall recovery is 88 $\pm$ 10%, n = 16. One of ACB's key problems with method RAM J/02/92 was the large interference peak(s) close to the rt < 9 minutes of clofentezine. In the revised method the rt of clofentezine is approximately 15.3 minutes and the interference peak(s) seem to be more removed from the analyte of interest.

In consultation with the lab in Beltsville (telcon on Dec. 11, 1995 between D. Griffith and H. Hundley) we concluded that the clean-up step has had a significant revision and now might be satisfactory to meet agency guidelines. We agreed a new tolerance method validation (TMV) is necessary to support this conclusion and to determine if all of our previous concerns have been addressed. The petitioner need not do a new ILV.

cc:R.F.,Circu.,Reviewer(FDG),PP#6F3392.
7509C:CBTS:Reviewer(FDG):CM#2:Rm804Q:305-5826:FDG:12/11/95:edit:fdg:12/18/95.
RDI:SecHd:RSQuick:12/14/95:BrSrSci:RALoranger:12/14/95:BrCh:MSMetzger:12/18/95.