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MEMORANDUM **[CONFIDENTIAL]**

SUBJECT: **Thifensulfuron methyl**. Dupont's 2/9/94 & 3/18/94 Responses [Analyses for Hexachlorobenzene & Pentachlorobenzene in the Technical; DPX-M6316] to the Agency 9/2/92 [10/2/92] HCB/PCB DCI, to S. Funk 8/6/93 Review; CBRS 11543, & to the Agency 3/17/94 Telephone Request & Agency 1/7/93, 7/26/93, 8/10/93 & 9/1/93 Letters. MRID No. 431473-01 & -02, CBRS No. 13423, DP Barcode No. **D200743**.

FROM: K. Dockter, Chemist
Special Review Section I
Chemistry Branch II, Reregistration Support
Health Effects Division (7509C)

THRU: Andrew R. Rathman, Section Chief
Special Review Section I
Chemistry Branch II, Reregistration Support
Health Effects Division (7509C)

TO: Richard Dumas / Dennis Utterback, PM Team 61
Special Review Branch
Special Review and Reregistration Division (7508W)

In response to the subject DCI, the cited review & cited Agency communications, Dupont Agricultural Products, has submitted a 13-page final report entitled, "Isolation and Quantitation of Pentachlorobenzene [PCB] and Hexachlorobenzene [HCB] from Thifensulfuron methyl [DPX-M6316] Technical Material" and "Supplement No. 1" [57 pages] thereto. The study, designated AMR 2668-93 and performed by Lancaster Labs., Inc. [LLI], Lancaster, PA, was completed on 01/26/94. No claim of CBI status was made for either the study or its supplement. However, this entire memorandum is classified **CONFIDENTIAL**, because of portions quoted herein from the cited review which was classified CONFIDENTIAL in its entirety.

In the cited review, S. Funk evaluated the analytical method protocol LLI Method #NS37003, and detailed nine required

changes/additions. They are reiterated below, followed by a

discussion of the current submission, and our conclusions and recommendation.

CONCLUSIONS:

1. Recoveries of the surrogate standard 1,2,3,4-tetrachlorobenzene [TCB] reportedly ranged from 92 to 109%.

2. Non-verifiable results claim that neither PCB nor HCB were detected at or above the LOQ, 100 µg/kg.

3. The analytical method NS-37-003 was not attached to the current study as claimed. Furthermore, the current study states that data calculations and transformations were performed as described in it. The results given cannot be verified without it.

4. Three of the 9 required protocol changes/additions were not followed.

RECOMMENDATION:

The registrant should be requested to provide a complete copy of analytical method NS-37-003, AND comply with ALL the protocol changes/additions. With regard to the latter, the following data/information are still required:

"1. The sampling plan must be detailed in the final report. The randomness of the lot selection process must be shown, and the extent of production (number of lots, production amount, production time period) represented by the seven or more lots must be presented."

5. For external calibration, the five-point curve must encompass the LOQ.

"6. An initial demonstration of acceptable accuracy and precision is required. A thifensulfuron methyl sample must be subdivided into four fractions. Each fraction must be fortified with PCB (100 µg/kg), HCB (100

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µg/kg), and surrogate and must be prepared and analyzed by the proposed method. The mean recovery of each compound plus/minus two standard deviations of the mean must fall in the range 70% - 130%. The protocol implies such a demonstration, but it is not described."

PM NOTE: The registrant should be given complete copies of this review.

Detailed Considerations

From S. Funk's review of CBRS No. 11543, dated 8/6/93, we reiterate:

"Conclusions

The following changes/additions are required for the analysis protocol for the determination of PCB and HCB in technical thifensulfuron methyl:

1. **The sampling plan must be detailed in the final report. The randomness of the lot selection process must be shown, and the extent of production (number of lots, production amount, production time period) represented by the seven or more lots must be presented.**

2. **A minimum of seven lots, not five, is to be sampled and analyzed.**

3. **A surrogate must be added to each sample and control prior to sample/control extraction and analysis, and the surrogate recovery is to be determined and reported. Target analyte values are NOT to be corrected for surrogate recovery.**

4. **Target analytes found by gc/ec to be present at apparent concentrations $\geq$ LOQ must be confirmed by gc/ms. Confirmation by a second column with gc/ec only will not suffice.**

5. For external calibration, a five-point curve is required, and the LOQ must be encompassed. The proposed three-point calibration is not acceptable.

6. An initial demonstration of acceptable accuracy and precision is required. A thifensulfuron methyl sample must be subdivided into four fractions. Each fraction must be fortified with PCB (100 µg/kg), HCB (100 µg/kg), and surrogate and must be prepared and analyzed by the proposed method. The mean recovery of each compound plus/minus two standard deviations of the mean must fall in the range 70% - 130%. The protocol implies such a demonstration, but it is not described.

7. The final report must contain copies of all sample and control chromatograms and the associated raw data (retention times, areas). Individual sample data (weight, final extract volume) must also be included. The information is to be properly labeled and arranged in chronological order.

8. The acceptance criteria for a sample and its MS are target analyte recoveries (MS) of 70% - 130% and a surrogate recovery rpd of $\leq$ 20%. The registrant may use more restrictive criteria generated from the initial demonstration of accuracy and precision and may substitute rpd's of target analyte recoveries between the MS and MSD for the sample/MS surrogate rpd. However, a MSD is not required.

9. Minimum acceptance criteria for the laboratory solvent blank and laboratory control sample are no target analytes present at or above the LOQ and no compounds present that interfere with the determination of the target analytes.

Recommendation

CBRS recommends that the registrant be requested to effect the

protocol changes noted in Conclusion Items No. 1 - 9 and then to proceed with the collection and analysis of seven or more lots of technical thifensulfuron methyl for PCB and HCB. Additional protocols need not be submitted."

The current study and its supplement are summarized below.

Approximately 0.05 g single samples from eight lots of 94% minimum active thifensulfuron methyl [DPX-M6316] were weighed into screw cap vials. Hexane [10 mL] and 10 mL concentrated sulfuric acid were added. Upon shaking, the PCB & HCB were partitioned into the hexane layer which was analyzed by gc/ecd. "Analytical method NS-37-003 is attached to this report." **It was not.**

The QC control substance was DPX-M6316 SR 12137, Reference No. B89/36, 98.4% active, expiration date 01/98. Recoveries of PCB & HCB spikes from control and a sample in duplicate were 106 & 114, 113 & 115, and 116 & 113%, respectively.

The sample results and surrogate recoveries are given in the following table.

Lot No.	Recovery %TCB	PCB µg/kg	HCB µg/kg
Reagent Blank	108.	<100	<100
Control Blank	104.	<100	<100
Control Spike	108.	220	203
C-930616-05B	102.	<100	<100
" MS	104.	221	204
" MSD	109.	214	188
C-930624-20A	92.	<100	<100
C-930630-30A	102.	<100	<100
C-930705-40C	98.	<100	<100
C-930710-50B	104.	<100	<100
C-930714-60B	97.	<100	<100
C-930719-70C	101.	<100	<100
C-930723-80B	100.	<100	10.

MS = Matrix Spike; MSD = Matrix Spike Duplicate

Clean hexane solvent injections showed that the small peak in Sample No. C-930723-80B, quantitated as 10. µg/kg HCB, did not represent contamination of the gc/ecd.

A PCB peak 3-5 times <LOQ was seen in all of the samples, including the reagent blank and control blank. Since clean hexane solvent injections showed that the gc/ecd was not contaminated, it is assumed to be a contaminant present during sample preparation.

The supplement completed on 2/17/94 contained the external standard curve, all sample and control chromatograms, and the parameters.

The five-point external standard curve given covers the range of "2.5 µg/l to 25. µg/l". Without further data/information, we are unable to verify whether this encompasses the LOQ.

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cc: K. Dockter, RF, SF, SR File.

RD/I ARRathman 9/15/95; RBPerfetti 9/15/95; EZager 9/19/95
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