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

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OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Identifying Number 034805. Ziram data call-in.
Submission of analytical method involving evolution of
carbon disulfide. MRID# 404952-01 [RCB# 3387]

FROM: Richard Loranger, Chemist *R. Loranger*
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THRU: Andrew Rathman, Section Head *ARR*
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TO: G. Werdig/F. Rubis, PM Team 50
Data Call-In Program
Registration Division (TS-767C)

The Agrichemicals Division of Pennwalt Corporation, on behalf of the Ziram Task Force, has submitted an analytical method for determining residues of dithiocarbamates on crops. The procedure entails generation of carbon disulfide, which is swept into a trap for colorimetric quantitation. RCB has stated in the past that such a method would be adequate for determining residues of ziram (R. Quick-2/4/87 and R. Loranger-12/21/87).

The submitted method is a copy of a publication in the Journal of the AOAC (Vol. 54, No. 3, 1971, pages 528-532, author George E. Keppel (FDA)). It is entitled "Collaborative Study of the Determination of Dithiocarbamate Residues by a Modified Carbon Disulfide Evolution Method". The procedure entails refluxing the crop with dilute HCl and SnCl₂. An air stream through the mixture carries evolved H₂S and CS₂ through a series of traps. The first one contains 10% NaOH solution and benzene (Pennwalt substitutes toluene) and traps the hydrogen sulfide. The second trap has an ethanolic solution of cupric acetate and diethanolamine. The evolved carbon disulfide forms a yellow complex [cupric salt of N,N-bis(2-hydroxyethyl) dithiocarbamic acid] whose absorbance is measured at 435 nm. Pennwalt notes that the samples should be cut while frozen and analyzed immediately.

The results obtained by 8 collaborators are tabulated in the publication. For 1-10 ppm zineb or ziram on grain the average recoveries were 77-92%. However, in 4 of the 6 sets of data, 1-2 values (35-55% range) were omitted as outliers. The paper concludes that "Further study on this method is recommended."

CONCLUSIONS AND RECOMMENDATION

The submitted method of carbon disulfide evolution should be adequate for gathering residue data for the parent compound ziram. The Task Force should be advised that the residue data supplied in response to the data call-in should include raw data (sample weights, volumes and absorbances of trap solutions, etc.) for control, treated and fortified samples of each crop so that we can verify reported residues and recoveries. Recovery data will be required on each crop to validate the method. We also advise that extra samples be kept frozen in the event that any metabolites of concern that would not be determined by carbon disulfide evolution are found in the plant metabolism studies.

cc: Circu, RF, PMSD/ISB, Loranger, Ziram SF
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