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

JUL 9 1986

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Triphenyl Tin Hydroxide, Response to Registration Standard: M&T Residue Analytical Method
EPA Reg. No. 8340-17
EPA File Symbol 5204-AO
[Accession No. 260289, RCB No. 813]
MRID 153228

FROM: Susan V. Hummel, Chemist
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THRU: Charles L. Trichilo, Chief
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TO: Henry Jacoby, PM #21
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M&T Chemicals, Inc. has submitted a residue analytical method for phenyltin species ($\emptyset_a SnX_{4-a}$) in sugarbeet, soybeans, peanuts, peanut hulls, pecans, carrots, and potatoes, in response to the Registration Standard for the fungicide triphenyltin hydroxide (TPTH). M&T has submitted validation data using triphenyltin hydroxide, diphenyltin chloride, and monophenyltin chloride as standards. No mention was made of tetraphenyltin. A similar method for sugarbeets was reviewed in our memo of 2/26/86 (S. Hummel, Accession No. 261251, RCB No. 127). The PM is filing this method under EPA Reg. No. 8340-17 (American Hoechst) since M&T does not have a registered product containing TPTH.

The Registration Standard for TPTH was issued on 9/30/85. M&T has previously submitted Product Chemistry data, which were reviewed in our memo of 8/16/85 (A. Reiter), and updated in our memo of 8/30/85 (A. Reiter). No additional data have been submitted to fill the remaining product chemistry data gaps.

Triphenyltin hydroxide is a fungicide registered for use on carrots, peanuts, pecans, potatoes, and sugarbeets. Tolerances have been established for residues of triphenyltin hydroxide, per se, in or on peanuts, pecans, and potatoes at 0.05 ppm, carrots and sugarbeets at 0.1 ppm, and peanut hulls

at 0.4 ppm (40 CFR 180.236). Tolerances for residues of TPTH on rice and soybeans are pending.

The metabolism of triphenyltin hydroxide in plants and animals is adequately understood. TPTH is not significantly absorbed or translocated in plants. The residue of concern is TPTH, per se, di- and mono- phenyltin oxides and hydroxides, and tetraphenyl tin. [redacted] residues of tetraphenyl tin could potentially concentrate on processing.

This submission (Accession No. 260789) contains the report, "Validation of a Method for the Separation and Determination of Phenyltin Species ($\emptyset_a SnX_{4-a}$) in Sugarbeets, Soyabeans (sic), Peanuts, Peanut Shells, Carrots, Pecans, and Potatoes by Liquid Chromatography/Atomic Absorption Spectroscopy," A. Marino, Oct. 23, 1985, M&T Chemicals, Inc. Method No. TA-45. The previously submitted method was designated M&T method No. TA-43.

These methods are reported to be applicable for the analysis fo TPTH and its degradation products (diphenyl tin oxide and phenyl stannoic acid) from agricultural crops at levels down to 50 ppb for M&T Method No. TA-43 and 10 ppb for M&T Method No. TA-45. It was not stated whether this level was ppb Sn or ppb TPTH. The tin compounds are extracted into an aqueous citrate buffer system, then extracted into hexane containing tropolone as a chelating agent. The tin compounds are then converted to the tetraorganotin compounds by reaction with butylmagnesium chloride (Grignard reagent). Triphenyltin hydroxide ($\emptyset_3 SnOH$) is converted to triphenylbutyltin ($\emptyset_3 SnBu$), diphenyltin oxide ($\emptyset_2 SnO$) is converted to diphenyldibutyltin ($\emptyset_2 SnBu_2$), and phenyl stannoic acid ($\emptyset_1 SnOOH$) is converted to phenyltributyltin ($\emptyset SnBu_3$). The tin compounds are separated by liquid chromatography using a reverse phase C8 column and an acetonitrile/ water/tetrahydrofuran (THF) isocratic solvent system. The LC parameters were adequately described. The separation is monitored by UV absorbance at 218 nm. Three minute fractions are collected. These fractions are then quantitated by graphite furnace (flameless) atomic absorption spectroscopy at 286.3 nm. Samples are injected into the AA in triplicate.

Triphenyltin hydroxide, diphenyltin dichloride, and monophenyltin trichloride are used to prepare fortified samples and standards. No explanation was offered for the use of the chlorides instead of the di- and mono- phenyltin hydroxides or oxides. The standards are dissolved in THF, reacted with butylmagnesium chloride to produce the phenylbutyltin compounds which are used as standards for the GF-AA. These standards are used to prepare a calibration curve to be used for quantitation. The sample calculations show that results are corrected for control samples. The sample preparation of the

Should that which may reveal the manufacturing process is not included.

controls was not described. It is unclear if the controls are plant controls or reagent controls.

Recoveries were reported for each crop matrix. Fortifications are apparently expressed as ppm $Ø_3SnOH$, $Ø_2SnCl$, and $Ø_1SnCl_2$ (approximately equal to ppm TPTH equivalents). Recoveries are corrected for controls. Tracings from the graphite furnace AA were included, along with raw data sheets. Controls showed residues approximately four to five times the residue level of the samples fortified at 50 ppb. Reported recoveries are tabulated below followed by recoveries uncorrected for controls.

Crop/Fortification Level (ppm TPTH equiv)	% Recovery $Ø_3Sn$	$Ø_2Sn$	$Ø_1Sn$
Sugar Beets			
0.5	100	109	87
0.1	84	98	80
0.05	113	103	71
Peanut Hulls			
1.0	94	102	98
0.4	115	92	85
0.2	112	112	95
0.1	113	128	95
Peanuts			
0.5	104	104	106
0.05	117	110	99
0.01	107	110	138
Soybeans			
0.5	105	96	93
0.1	98	108	89
0.05	88	114	93
0.02	99	115	115
Carrots			
0.5	107	102	86
0.1	93	100	83
0.01	121	82	84
Pecans			
0.5	97	96	90
0.05	96	94	84
0.01	96	100	93
Potatoes			
0.5	99	105	100
0.1	80	100	105
0.01	118	101	111

Without correcting for controls, the recoveries would be as follows:

Crop/Fortification Level (ppm TPTH equiv)	% Recovery $\emptyset_3$Sn	$\emptyset_2$Sn	$\emptyset_1$Sn
Sugar Beets			
0.5	132	138	116
0.1	235	217	318
0.05	440	379	857

Similar recoveries would be calculated for the other crops without correcting for controls. The recoveries calculated above are unacceptably high.

CONCLUSIONS

We recognize that additional methodology and residue data have been submitted and will be reviewed shortly. Upon review of the additioonal data our conclusions may change.

1. It was not clear whether the stated limit of detection was expressed as ppb Sn or ppb TPTH. It appears that the limit of detection was intended to be expressed as ppb TPTH. This should be clarified. The stated limit of detection may or may not be adequate to enforce tolerances after they are reevaluated to include the mono-, di-, and tetra- phenyltin species.

2. The sample treatment of the control samples was not described. It is unclear if the controls were plant controls or reagent control. RCB normally does not accept residue analytical methods requiring correction for untreated control samples, since untreated control samples are not available for enforcement purposes. The recoveries calculated without correction for control samples are unacceptably high.

3. Diphenyltin oxide or hydroxide and monophenylstannoic acid should be used for the preparation of the standards and fortified samples. Alternatively, the registrant should demonstrate that the di- and mono- phenyltin chlorides have recoveries and responses comparable to those of the oxides and hydroxides. Sources of the standards for TPTH and mono- and di- phenyltin species should be stated. These standards should be made available from the EPA Pesticide Repository.

4. The registrant should demonstrate that the method is applicable to the determination of tetraphenyltin, since residue data reflecting analysis for tetraphenyltin are required for processed commodities of sugarbeets, potatoes, and peanuts.

5. No data were submitted to demonstrate that other organotin pesticides will not interfere in this determination. These data are needed.

6. This method would not be suitable for the analysis of TPTH and its metabolites in meat, milk, poultry, and eggs, since a base hydrolysis step has not been included. An analytical method for the analysis of TPTH and its metabolites in meat, milk, poultry and eggs is still needed.

7. Storage Stability data were not included in this submission. These data are needed.

RECOMMENDATIONS

We recommend that the registrant be informed of our conclusions and advised to submit data to satisfy the deficiencies outlined in our conclusions. We recognize that our conclusions may change upon review of the additional data recently received.

cc: R.F., Circu., S. Hummel, Triphenyltin Hydroxide SF, Triphenyltin Hydroxide SRF (Hummel), Reg. Std. File (W. Boodee), PM#31, PMSD/ISB
RDI: EZ:7/03/86:RDS:7/07/86
TS-769C:RCB:SVH:svh:Rm.710A:CM#2:557-3045:7/09/86