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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460
AUG 8 1988

MEMORANDUM

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

SUBJECT: Monsanto submission of proposed regulatory enforcement Method in response to Alachlor Registration Standard [MRID No. 405580-01, RCB No. 4112]

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The Product Manager has requested review of Monsanto's proposed enforcement method for alachlor. RCB recently requested a method validation from BUD/COB for this method (See S. Hummel memo of 7/21/88).

Tolerances have been established for alachlor and its metabolites in or on peanuts and other commodities. Alachlor [2-chloro-2',6'-diethyl-N-(methoxymethyl) acetanilide] is the active ingredient in LASSO Herbicide. Alachlor metabolites include those containing the diethylaniline (DEA) moiety and those containing the hydroxyethylethylaniline (HEEA) moiety.

Monsanto Company has submitted proposed analytical enforcement methodology for alachlor and its DEA and HEEA metabolites on raw agricultural commodities in response to the Alachlor Registration Standard. Previously submitted analytical methodology used glassware which was not commercially available or a chromatographic detector which was not available in the EPA or FDA District Laboratories.

This analytical method is different from previously submitted methods. It does not require the use of any custom made glassware used in previous methods. The sample workup is similar to that used with the custom made distillation apparatus. In this method, the distillation apparatus is made of stock glassware pieces. Following steam distillation and separation of DEA and HEEA, the DEA and HEEA are cleaned up on a disposable

aminosilica column, and collected as separate fractions. The DEA is not derivatized. The HEEA is derivatized with acetyl chloride. DEA and HEEA-acetate are quantitated by Gas Chromatography with nitrogen selective detection. The method is describee below in greater detail.

"Regulatory Enforcement Method for the Determination of Alachlor Residues in Raw Agricultural Commodities," A. G. Hackett, L. R. Holden, and J. A. Graham, Monsanto Agricultural Company Report No. MSL-7601, Monsanto R. D. No. 861, March, 1988, EPA MRID No. 405580-01.

Samples are extracted with 20% water/acetonitrile. The solvent is evaporated to near dryness. The extract is hydrolyzed in base to produce DEA and HEEA. The DEA and HEEA are steam distilled in a hydrolysis assembly assembled from stock glassware pieces, with joints sealed with teflon sleeves or teflon heat shrink tubes. The DEA and HEEA produced are collected in acid. (takes about 1 hour) The distillate is neutralized, made basic, and the DEA and HEEA partitioned into methylene chloride. The extract is solvent exchanged with iso-octane, and the DEA and HEEA are separated and cleaned up using a disposable aminosilica solid phase extraction column. The column is washed with methylene chloride and then isooctane. The DEA is eluted with ethyl acetate/isooctane, and the HEEA is eluted with methylene chloride. The isolated 2,6-HEEA is derivatized with acetyl chloride. The DEA is not derivitized. Quantitation is by GC/NPD in 2 separate runs. A 6' 10% DC200 column is used for the isothermal separation. Calculations were described. Results are expressed as alachlor equivalents.

2,6-Diethylaniline (available from Aldrich) and 2-(1-Hydroxyethyl)-6-ethylaniline (synthesized in-house) are used as standards. Two metabolites, sodium salt of 2-[(2,6-diethyl-phenyl) (methoxy-methyl)amino]-2-oxo-ethane sulfonic acid (tertiary amide sulfonic acid metabolite, containing 2,6-DEA moiety), and N-[2-(1-hydroxyethyl)-6-ethylphenyl]-N-(methoxymethyl)-2-(methylsulfonyl) acetamide (hydroxyethyl tertiary amide sulfone metabolite containing 2,6-HEEA moiety), are used for fortification and recovery calculations.

The limit of method validation, (i.e., the method was not validated below this level) is reported to be 0.025 ppm in all commodities. (The method was validated for soybean, corn, and peanut commodities.) The limit of detection (LOD) was reported to be 0.015 ppm. Undated sample chromatograms for standards; and one check sample, one sample fortified at the limit of method validation, and one sample fortified at a higher level for each commodity were included with the analytical method. Formulas for sample calculations were included. Recoveries were determined and reported as follows.

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RECOVERIES (%)

Commodity	2,6-DEA range	2,6-DEA average	2,6-HEEA range	2,6-HEEA average
corn forage	72-103	87	66-91	78
corn stover	78-118	91	55-117	86
corn grain	63-132	90	49-125	93
soybean forage	72-116	92	66-121	90
soybeans	71-125	90	65-117	88
peanut hay	90-101	95	76-105	91
peanut w/ hull	58-98	81	74-122	101

Conclusions and Recommendation

This analytical method does not require the custom made glassware needed for previous alachlor methods. Additionally, it uses a detector more commonly available than the electrochemical detector used in the alachlor method which most recently evaluated in our laboratory. We have recommended that this method be evaluated by BUD/COB. (See S. Hummel memo of 7/21/88.)

cc: RF, circu, S. Hummel, Alachlor Reg. Std File (Boodee), PMSD/ISB
RDI:EZ:08/08/88:RDS:08/08/88
TS-769:RCB:SVH:svh:RM810:CM#2:x77324:08/08/88