10-26-94

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

OCT 26 1994

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

MEMORANDUM:

SUBJECT: PP#8F3607: Glufosinate-Ammonium: Results of Petition Method Validation for Parent and Metabolite in/on Animal Tissue Commodities.

FROM: Joel Garbus, PhD., Chemist
Tolerance Petition Section III
Chemistry Branch Tolerance Support (7509C)

THRU: R. A. Loranger, PhD, Acting Chief
Chemistry Branch Tolerance Support
Health Effects Division (7509C)

TO: J. Miller / J. Mayes, PM-23
Registration Division

Hoechst-Celanese had petitioned for permanent tolerances for the herbicide glufosinate-ammonium, (Ignite), and its metabolite, 3-methylphosphinicopropionic acid, in/on almond hulls at 0.5 ppm; apples, grapes and nuts at 0.05 ppm; cattle fat, cattle meat, eggs, goat fat, goat meat, horse fat, horse meat, poultry meat, poultry fat, sheep fat, and sheep meat at 0.05 ppm; cattle mbyp, goat mbyp, horse mbyp, poultry mbyp, and sheep mbyp at 0.10 ppm; and milk at 0.02 ppm. The need for these requested tolerances for meat, milk, and eggs arose from the potential of feeding treated almond hulls. However, the petitioner had not submitted a validated method for animal tissues and the tolerance requests were denied.

The petitioner responded by: 1) submitting revised Sections B and F that removed the use on almonds and dropped almonds and almond hulls from proposed tolerances, 2) dropping the tolerance requests for animal tissues, milk, and eggs, and 3) submitting independently validated analytical methods for animal tissues, milk, and eggs for validation by the Agency. [The method for plant matrices (apples, grapes, almond nutmeats and hulls, soybeans, and corn grain, fodder and forage) had been validated by the Agency] .

With these amendments of the original petition, CBTS could now recommend for the use of glufosinate on apples and grapes with

tolerances for these commodities at 0.05 ppm and for nuts (except almonds) at 0.10 ppm. Tolerances for the entire nut group could be reproposed along with tolerances for meat, milk, poultry, and eggs once the method had been validated by the Agency.

CBTS requested that a method validation be initiated for the determination of glufosinate-ammonium and its metabolite in/on animal tissue commodities which, if successful, would permit the establishment of the requested tolerances on the nut crop group and animal commodities (J. Garbus, memo, 1/24/94). The method for animal tissue commodities had been developed and independently validated by the petitioner since the submission of the original petition (see above). Normally we request method validation at 1x and 2x the requested tolerances. In this instance we have asked for 1x and 5x so as to make the Agency's validation comparable to the petitioner's independent validations.

The Analytical Chemistry Section has completed its validation and has forwarded their results and comments to CBTS (J. Negron, memo, 9/27/94).

CBTS' Conclusion and Recommendation

1. The method will be acceptable as an enforcement method if the suggestions of ACL report and of the TMV pre-review (see below) are incorporated into the method. If additional specific details regarding the ACL suggestions are needed, the petitioner should consult the chemists at ACL.

2. An analytical standard only for the metabolite is at the EPA Repository. Standards for the parent and metabolite and their derivatized forms are available from Hoechst-Celanese Corp., Somerville, NJ. The petitioner should provide these standards to the Repository.

3. Upon the satisfactory completion of the above requirements, CBTS can recommend for the establishment of the requested tolerances for the nut crop group and for the meat, milk, and egg tolerances. The petitioner should submit a revised description of the method incorporating the suggestions of the ACL and an amended Section F requesting tolerances for the nut crop group (without the exception for almonds) and for the animal commodities.

Results

MTO REPORT

Commodity	Chemical Added	Level Added ppm	Found ppm	Recovery %
Milk	control	---	N.D.	
Milk	control	---	N.D.	
Milk	glufosinate	0.021	0.021	100
Milk	glufosinate	0.021	0.027	129
Milk	glufosinate	0.106	0.132	125
Milk	glufosinate	0.104	0.133	128
Milk	Metabolite[1]	0.021	0.021	100
Milk	Metabolite[1]	0.021	0.021	100
Milk	Metabolite[1]	0.104	0.098	94
Milk	Metabolite[1]	0.104	0.096	92
Eggs	control	---	N.D.	
Eggs	control	---	N.D.	
Eggs	glufosinate	0.066	0.077	117
Eggs	glufosinate	0.066	0.075	114
Eggs	glufosinate	0.27	0.215	80
Eggs	glufosinate	0.27	0.257	95
Eggs	Metabolite[1]	0.065	0.049	75
Eggs	Metabolite[1]	0.065	0.047	72
Eggs	Metabolite[1]	0.26	0.208	80
Eggs	Metabolite[1]	0.26	0.232	89
Meat (Original Method)				
Beef Muscle	control	---	0.020	
Beef Muscle	control	---	0.011	
Beef Muscle	glufosinate	0.048	0.056	117
Beef Muscle	glufosinate	0.048	0.043	90
Beef Muscle	glufosinate	0.27	0.535	198
Beef Muscle	glufosinate	0.25	0.588	218
Beef Muscle	Metabolite[1]	0.047	0.058	123
Beef Muscle	Metabolite[1]	0.047	0.066	144

ommodity	Chemical Added	Level Added	Found	Recovery

		ppm	ppm	%
Beef Muscle	Metabolite[1]	0.26	0.291	112
Beef Muscle	Metabolite[1]	0.26	0.335	129
Meat (Method as Modified by ACL)				
Beef Muscle	control	---	N.D.	
Beef Muscle	control	---	N.D.	
Beef Muscle	control	---	N.D.	
Beef Muscle	control	---	N.D.	
Beef Muscle	glufosinate	0.047	0.053	113
Beef Muscle	glufosinate	0.047	0.058	123
Beef Muscle	glufosinate	0.066	0.063	96
Beef Muscle	glufosinate	0.066	0.061	92
Liver	Metabolite[1]	0.09	0.12	133
Liver	Metabolite[1]	0.093	0.112	120
Liver	Metabolite[1]	0.093	0.091	98
Liver	Metabolite[1]	0.092	0.102	111
Liver	Metabolite[1]	0.13	0.132	102
Liver	Metabolite[1]	0.13	0.155	119
Liver	Metabolite[1]	0.51	0.484	95
Liver	Metabolite[1]	0.51	0.580	114
Liver	Metabolite[1]	0.51	0.484	95
Liver	Metabolite[1]	0.53	0.602	114
Liver	Metabolite[1]	0.53	0.559	113
Liver	Metabolite[1]	0.52	0.669	129
Liver	Metabolite[1]	0.52	0.557	107

ommodity	Chemical Added	Level Added ppm	Found ppm	Recovery %
Liver (Method as Modified by ACL)				
Liver	control	---	N.D.	
Liver	control	---	N.D.	
Liver	glufosinate	0.17	0.17	100
Liver	glufosinate	0.17	0.16	94
Liver	Metabolite[1]	0.13	0.099	76
Liver	Metabolite[1]	0.13	0.107	82

[1] Metabolite = 3-methylphosphinicopropionic acid

Modifications to method (major or minor):

Special precautions to be taken: None

Source of analytical reference standards: The petitioner (HRAV)

If derivitized standard is used, give source: The petitioner (HRAV)

Instrumentation for quantitation: GC/FPD

Instrumentation for confirmation: N/A

If instrument parameter differ from those given in method, list parameters used: N/A

Commercial sources for any special chemicals or apparatus:

Comments:

ACL's comments about and suggested modifications to the method are paraphrased below.

1. The liver and meat extracts caused interferences at the retention time peak for the parent. This could be avoided by modifying the silica gel cleanup step as described below.

a. The major modifications to the method that led to satisfactory recoveries were the substitution of the silica cartridge with a 12 mm id X 240 mm glass column dry packed with 10.5 grams of a similar packing material [silica Gel 60, particle size 0.063-0.200 mm (70-230 mesh ASTM)] and the procedure for the calibration the cleanup column. Columns were conditioned by using equivalent volumes to those described in the original method (Section 7.6.1)

b. For liver, columns were calibrated by adding 100 ml of the eluting solvent and analyzing 5 ml fractions. Separate fractions had to be collected for parent and metabolite.

c. For meat, the column was calibrated by collecting 1 fraction of 14 ml, 12 fractions 3 ml each, and then 7 fractions of 5 ml each.

2. ACL used a 15 meter x 0.53 mm DB-WAX gas chromatograph column for all matrices. The method as described used an 8 meter column. The petition should revise the method to indicate that a 15 meter column can be used.

3. The literature included with the Aldrich Gold Label methyl acetate used at ACL cautions about the moisture sensitivity of this solvent. The method should make reference to this potential problem. Aldrich's literature details a technique to avoid moisture. The method should note that Aldrich's reagent-grade methyl acetate is packed in Sure/Seal packages under nitrogen. The needed amount of reagent is to be removed by syringe through a septum in the seal.

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.. The glass liner of the instrument needs to be changed as soon as signs of loss of sensitivity and deterioration are detected.

5. The length of time to analyze a set of 6 samples is about 24 hours including instrument runs.

6. The estimated sensitivities were found to be 0.02 ppm for eggs, 0.005 ppm for milk, and 0.03 ppm for meat and liver.

7. An analytical standard for the metabolite is available from the EPA repository. Standards for the parent and metabolite and their derivitized forms are available from Hoechst-Celanese Corp., Somerville, NJ. The petitioner should provide these standards to the repository.

8. Sample preparation: A sample preparation procedure for eggs should be described. As the egg sample preparation is the same as that for animal and poultry tissues, the term "eggs" should be included in the heading of the sample preparation section relating to meat and poultry tissue extraction.

9. Anion Exchange Cleanup: A statement should be included as to whether the column stop-cock should be closed after the 75 ml of water has reached the top of the column. For ACL's successful validation the procedure was to keep the stopcock partially opened to allow for a drip rate of 1 to 2 drops per second. This procedure is given in the description of the method for plant matrices and should be included in the description of the animal tissue methods.

10. Chromatography of milk samples: The septum purge flow and the inlet timing should be described. Values for the operating parameters for GC determination of glufosinate residues are given for other matrices. ACL used similar settings, i.e, those for meat, initially in examining the milk samples. The description of the method does state that optimum settings for a particular matrix using a particular column need to be determined empirically. However, the revised description should include suggested settings for the analysis of milk samples.

11. The method will be acceptable as an enforcement method if the suggestions in this report and those of the TMV pre-review are incorporated into a revised description of the method.

cc: R.F.; Circ.; M. Bradley (PAM-2 editor);MTO F; Garbus; PP#8F3607:
H. Hundley (BEAD)
RDI:PE:10/18/94:MF:10/20/94:RAL:10/20/94
7509C:CBTS:JG:jg:10/20/94:CM#2:805b:703 305-5405