3M Manufacturing Facilities
Analysis of Alfalfa Harvested from 3M Cordova, Illinois Plant Facility

Executive Summary
3M Environmental Laboratory

June 21, 2001

In the fall of 2000, samples of alfalfa being grown on the 3M Cordova Plant (Cordova, Illinois) property were collected by plant personnel. There was no sampling plan in place prior to harvest. No documentation was made of sampling procedures, locations, or handling. The alfalfa was submitted for analysis of methyl FOSE alcohol, ethyl FOSE alcohol, PFOS, PFOA, and PFOSA. The method developed for the extraction and analysis of green beans was adapted to use on the alfalfa. The QC samples included with the sample analyses indicated that a true blank matrix was not used for spiking, and that recoveries were occasionally unacceptably low. For all of the reasons listed above, interpretation of analytical results from these alfalfa samples is not recommended.

All of the alfalfa grown at the 3M Cordova Plant property was landfilled after harvest.

ALFALFA SUMMARY

SPONSOR
3M Environmental Technology and Safety Services
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DATA REQUIREMENTS
Non-GLP

TESTING LABORATORY
Centre Analytical Laboratories, Inc. (Centre)
3048 Research Drive
State College, PA 16801
Phone 814-231-8032

CENTRE IDENTIFICATION NUMBER
023-046

1. PURPOSE

The purpose of this study was to find the amount of MeFOSE-OH, EtFOSE-OH, PFOS, PFOSA and PFOA in alfalfa samples using the method titled "Method of Analysis for the Determination of Fluorochemicals in green beans, apples, pork muscle, cow milk, chicken muscle, chicken eggs, bread, hotdogs, and catfish by LC/MS/MS."

2. TEST MATERIALS

The following analytical standards were used:

Test Material	Lot or TCR Number	Purity (%)	Expiration Date
MeFOSE-OH	NA	NA	01/01/10
EtFOSE-OH	Purified from Lot 30107	TBD	04/07/01
PFOS	TCR00017-46	97.9	08/31/01
PFOA	332	TBD	07/06/01
PFOSA	L-15709	95.1	02/15/01

TBD= To be determined

Note: GLP characterization data for MeFOSE-OH, EtFOSE-OH, PFOA and PFOSA was unavailable at the time of standard preparation. Therefore, PFOS was the only analyte corrected for percent purity when preparing standard solutions.

3. SAMPLE PROCESSING AND IDENTIFICATION

All samples were processed with dry ice in a Hobart food processor.

The samples were labeled as follows:

Client Sample ID	Centre ID	Description
14978	0009591	Control Alfalfa
14979	0009592	Alfalfa Sample
14980	0009593	Alfalfa Sample
14981	0009594	Alfalfa Sample

4. ANALYTICAL METHOD

The samples will be analyzed according to the analytical method titled "Method of Analysis for the Determination of Fluorochemicals In Green Beans, Apples, Pork Muscle, Cow Milk, Chicken Muscle, Chicken Eggs, Bread, Hotdogs, and Catfish by LC/MS/MS" following the green bean extraction steps. (see Appendix for a copy of the method).

5. EXPERIMENTAL DESIGN

1. A reagent blank, a control and two spikes of control alfalfa were extracted following the green bean extraction steps of the method entitled "Method of Analysis for the Determination of Fluorochemicals In Green Beans, Apples, Pork Muscle, Cow Milk, Chicken Muscle, Chicken Eggs, Bread, Hotdogs, and Catfish by LC/MS/MS" in order to verify that the green bean extraction would sufficiently work on alfalfa. See **Attachment 1: Data set 100600.**

2. A reagent blank, a control, 2 recovery spikes (control alfalfa spiked at 0.5 ng/g and at10.0 ng/g) and duplicate portions of the 3 remaining alfalfa samples were extracted and analyzed according to the method listed in experiment 1. See **Attachment 2: Data set 100900 Alfalfa.**

3. Experiment 2 was repeated but spiking was done at 5.0 ng/g and 20 ng/g for EtFOSE-OH, MeFOSE-OH, PFOSA and PFOA. Since the amount of PFOS found in the control samples in experiment 2 was ~30 ng/g the spiking for PFOS was done at 50 ng/g and 200 ng/g in order to ensure that recoveries could be calculated. See **Attachment 3: Data set 101100 Alfalfa and Dilution Data set 101100R Alfalfa.**

4. A reagent blank, 2 reagent spikes (one at 1.25 ng/mL and the other at 50 ng/mL), an alfalfa sample and an alfalfa sample spiked at 10 ng/g) was extracted according to the method listed in experiment 1 with the following changes to the column cleanup:
   a. Section 4.3.4 of the method: a pre-packed carbon column from supelco was used instead of the florisil/silica gel/carbon/LC-NH2 column.
   b. Section 4.3.4 of the method: The column was conditioned with 10 mL of saturated ascorbic acid, followed by 10 mL of ACN.
   c. Section 4.3.1 step c of the method: After all fractions had been placed through the carbon column, the column was washed with 10 mL of ACN followed by 20 mL of 90:10 ACN:2% ascorbic acid in methanol. The wash was also collected into the same flask as the original extract and the method continued with step e.

   See **Attachment 4: Data set 101300 Test.**

6. RESULTS

1. Experiment 1 results:

		% Recovery				
Sample ID	Fort Level	EtFOSE-OH	MeFOSE-OH	PFOS	PFOSA	PFOA
0009591 Spk A	5.0 ng/g	85	95	38	68	52
0009591 Spk B	20 ng/g	96	98	63	63	65

Even though recoveries for PFOS, PFOSA and PFOA seemed low it was thought that the method as written for green beans would sufficiently work on alfalfa.

2. Experiment 2 results:

		% Recovery				
Sample ID	Fort Level	EtFOSE-OH	MeFOSE-OH	PFOS	PFOSA	PFOA
0009591 Spk A	0.5 ng/g	85	103	41	71	94
0009591 Spk B	10 ng/g	73	78	-53	62	53

The recoveries for PFOSA and PFOA were still a little low. Being that there was more PFOS in the blank than the level that was spiked, recovery numbers for PFOS were inaccurate. It was decided to repeat the experiment using a higher spiking level for PFOS.

3. Experiment 3 results:

		% Recovery				
Sample ID	Fort Level	EtFOSE-OH	MeFOSE-OH	PFOS	PFOSA	PFOA
0009591 Spk A	5.0 ng/g	92	97	85*	78	127
0009591 Spk B	20 ng/g	98	96	102*	65	54

* PFOS was spiked at 50 and 200 ng/g.

Sample results:

		Analyte Found (ng/g)				
Centre Sample ID	Client ID	EtFOSE-OH	MeFOSE-OH	PFOS	PFOSA	PFOA
0009591 Blank A	14978	0.153	0.135	54.9	0.439	2.54
0009592	14979	0.201	0.0818	53.8	0.124	1.08
0009592 Dup	14979	0.582	0.0852	54.9	0.322	1.09
0009593	14980	0.235	0.182	245	0.164	1.94
0009593 Dup	14980	0.293	0.186	275	0.205	5.25
0009594	14981	0.144	0.137	41.1	0.0590	3.67
0009594 Dup	14981	0.135	0.128	42.8	0.0575	1.78

Even though the high spike for PFOA was low, the PFOA results were still accepted based on the fact that the low spike was acceptable and all PFOA residues found were at the same level or lower than the low spike level.

4. Experiment 4 results:

		% Recovery				
Sample ID	**Fort Level**	**EtFOSE-OH**	**MeFOSE-OH**	**PFOS**	**PFOSA**	**PFOA**
Reagent Spk A	1.25 ng/mL	107	85	0	82	51
Reagent Spk B	50 ng/mL	87	88	55	83	76
0009594 Spk C	50 ng/mL	20	18	65	45	33

It appears that the alternative clean up did not improve the recoveries for the samples containing matrix.