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EPA East – Room 6428 Attn: Section 8(e)
United States Environmental Protection Agency
Office of Pollution Prevention and Toxics
1200 Pennsylvania Avenue, N. W.
Washington, D. C. 20460-0001

Re: TSCA Section 8(e) Substantial Risk Notice: Sulfonate-based and Carboxylic-based Fluorochemicals, Docket 8EHQ-0598-373 – Fluoropolymer Generation Test Method Development Experiments

Dear Sir or Madam,

On February 26, 2010, 3M provided to the EPA a TSCA 8(e) submission summarizing data generated by 3M on behalf of the Fluoropolymer Manufacturers Group (FMG). This information resulted from Generation Test Method Development experiments aimed at developing a method to test whether fluoropolymers are capable of “generating” perfluorooctanoic acid (PFOA) when heated to just below the onset of its melting point. As 3M indicated it would do in that notice, we are now enclosing the recently finalized third report which details the method development work carried out from May 2008 through July 2009.

Although 3M does not believe that these results satisfy the “substantial risk” reporting threshold, we recognize the ongoing work by U.S. EPA to assess fluorochemical exposure pathways, and therefore, are placing a notification of these results in the 8(e) docket.

If you have any questions, please do not hesitate to contact Jeanette McCauley at (651) 733-9383 or jamccauley2@mmm.com.

Sincerely,

Jean B. Sweeney (JBS)

Jean B. Sweeney
Staff Vice President, Environmental Health and Safety Operations

Enclosure

CONTAINS NO CBI

2009 Annual Report on Method Development for PFOA Generation Testing

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I. INTRODUCTION

Over the past 5 years, the Fluoropolymer Manufacturers Group of the Society of the Plastics Industry (FMG) has carried out a series of experiments to assess whether perfluorooctanoic acid (PFOA) is generated from the test substance (a PTFE composite) exposed to very high temperatures. These experiments included two main elements: first, the development of sample handling techniques to measure PFOA residuals in the test substance at sub part per billion levels, and second, the development of the thermal test method that included design of new equipment and procedures. This work was performed by 3M Company and Dyneon LLC on behalf of the FMG.

Since the beginning of this program, the FMG has informed EPA of the progress through reports and technical discussions. The first report was submitted to the US EPA in April 2007, and the second was submitted in September 2008. These reports covered work done from late 2005 through May 2008.

This third report on method development covers work carried out from May 2008 to July 2009, and presents information about the techniques used to perform the necessary experimentation, and summarizes the results of those experiments. Specifically, the report includes:

- ⇒ A discussion of the protocol, procedures and results of accelerated solvent extractions (ASE) to determine whether background PFOA was present in the test substance used in the thermal tests, and
- ⇒ The further development and final design of equipment to perform the thermal test, the results of some testing done with the original design of the test system, and the results of initial testing using the redesigned equipment.

The test substance used in ASE and the thermal testing methods was a mixture of suspension grade PTFE supplied by the FMG member companies that was manufactured without using a PFOA emulsifier. Two types of suspension grade PTFE were included in the Test Substance, standard PTFE and modified PTFE. Experiments were performed on the test substance as received (Test Substance 1) and as re-mixed (Test Substance 2) as well as after the test substance had been ASE solvent washed and cryomilled.

In addition, the thermal test apparatus was redesigned to include a simultaneous blank, which allowed for improvements in the analytical methodology to reduce the lower limit of quantitation (LLOQ). Data generated in this report and shown in Tables 14-19 were based on the redesigned test apparatus. Thermal test data in earlier Tables were generated using the original single reaction flask equipment configuration.

This report details analytical results for each of the above-mentioned test substance types relative to PFOA and, for some experiments, also for other perfluorocarboxylic acids (PFCAs). To simplify the report, data are not always presented in chronological order.

The overall goal of the work has been to develop a reliable method to assess whether PFOA would be released from the test substance, when heated to 315° C for 24 hours in a stream of humidified air. This necessitated developing the ability to quantify the amount of PFOA released. This program has required new analytical methodologies and unique concepts and equipment, and as a result, has presented significant challenges that have necessitated new approaches.

Throughout this report the analytes of interest are referred to as “acids”. This term is inclusive of both the free acid and various salts of the free acid, such as the ammonium salt. It should be noted that the actual species being quantified is the anion of the acid. In the case of PFOA, the anion is the perfluorooctanoate anion. In addition, testing was also performed for other homologues of PFOA, namely PFHxA, PFNA and PFDA. The analytical techniques used in this study are not able to identify the cation associated with the anion in its dissociated state.

II. KEY ASPECTS OF METHOD DEVELOPMENT EXPERIMENTS

A. Accelerated Solvent Extraction

Accelerated solvent extraction (ASE) is a fully automated technique that uses common solvents to extract solid and semisolid samples rapidly. ASE operates at temperatures above the normal boiling point of most solvents, using pressure to keep the solvents in liquid form during the extraction process. Typically, ASE methods are completed in 15–25 min, while consuming only 15–50 mL of solvent. ASE was introduced in 1995 by Dionex Corporation and is recommended under US EPA Methods 3545 and 3545A for extraction of organophosphorus pesticides. In this method development the Test Substance was extracted using methanol as the solvent with the cells being maintained at 150 degrees C and 1500 pounds per square inch of pressure applied.

B. Thermal Test Apparatus

1. Single Reaction Flask and Impinger Train

The single reaction flask and impinger train system is an instrument configuration that utilizes a single, pre-heated inlet gas source connected to a single reaction flask within the heated zone (oven). This set up uses a glass transfer line from the reaction flask within the oven connected to a set of two impingers in series. The impingers are outside the heated zone and are maintained at zero degrees C by immersing the impingers in an ice bath. The impinger train exhaust was passed through an XAD resin trap placed in the exit air stream flow to collect any material of interest not captured in the aqueous matrix within the dual impingers. See Figures 1 & 2.

2. Dual Reaction Flask and Impinger Train

The dual reaction flask and impinger train system is an instrument configuration that has a single, pre-heated inlet gas source connected to a stream splitter allowing two reaction

flasks to be used in the oven. This set up uses two glass transfer lines from the reaction flasks within the oven connected to two separate sets of two impingers each connected in series. Both sets of impingers are maintained at zero degrees C by immersing the impingers in an ice bath. The impinger train exhausts through an XAD resin material trap placed in the exit air stream flow to collect any material of interest not captured in the aqueous matrix within the dual impingers. Two gas flow meters are attached to the exit air streams allowing operators to balance the flow equally through both reaction flasks and impinger sets. See Figure 4.

3. Standard Conditions

Many of the experiments were performed under the following standard conditions developed during dialogue between US EPA and the FMG:

- ⇒ Temperature: The temperature for testing was set at 10 degrees C below the onset of the melting point of the test substance as determined by differential scanning calorimetry (DSC). This temperature was determined by triplicate testing using DSC to be 315 degrees C.
- ⇒ Time interval: The standard time interval was set at 24 hours duration.
- ⇒ Percent relative humidity: The percent relative humidity was set at 50% relative humidity.
- ⇒ Carrier gas and flow rates: The standard test carrier gas was zero grade air maintained at a constant flow rate of 100 milliliters per minute.

4. Other Conditions

Conditions other than the above standard conditions are described in the text as necessary and include all other operational conditions as described other than the standard operational conditions.

C. Analytical Approach and Progress

1. Instrument Minimum Detectable Limit

Most analytical instruments produce a signal even when a blank (matrix without analyte) is analyzed. This signal is referred to as the noise level. The instrument detection limit is the analyte concentration that is required to produce a signal greater than three times the standard deviation of the noise level. This may be practically measured by analyzing eight or more standards at the estimated instrument detection limit and then calculating the standard deviation from the measured concentrations of those standards. This is then used to establish an instrument detection limit which does not include the matrix or the extraction variations of the method. As such, the instrument detection limit value is of limited value for purposes of meaningful quantitation.

2. Minimum Detectable Limit (Method)

The method minimum detectable limit (MDL) is affected by any additional steps completed during an analysis. These other necessary method steps (such as: dilutions, extractions, solution transfers, concentration steps) all add additional opportunities for error. Since detectable limits are defined in terms of error, this will naturally increase the measured detectable limit. This detectable limit (with all steps of the analysis included) is called the method minimum detectable limit (MDL).

3. Lower Limit of Quantitation (LLOQ)

The lower limit of quantitation (LLOQ) is the limit of concentration at which one can reasonably tell the difference between two different values. The LLOQ can vary dramatically between different labs. Overall, the LLOQ is approximately 5 times the minimal detectable limit (MDL) and is generally the lowest point that is fitted on the extracted standard curve where the curve itself produces acceptable regression values including that point. Specifically, in this project work the LLOQ is established by the lowest point included in the regression analysis of the matrix matched, full method extracted standard curve.

4. Values between LLOQ and the minimum detectable limit (MDL)

Values less than the LLOQ can not be accurately quantitated as one can not distinguish between any two different values reasonably (within acceptable variation) by definition. Therefore, values falling between the LLOQ and MDL of the method can not be reported as concentration values.

5. Blank Corrected Totals

Tables that include “corrected total concentrations” have actual measured blank concentrations above the LLOQ. The results that have the value of the “blank” reaction flask result subtracted from that of the “test substance” reaction flask are considered “blank corrected” results.

Results from the single reaction flask system all had blank runs completed where the results were less than 0.5 ng/g (the LLOQ). Therefore, all results in the tables completed using the single reaction flask instrument set-up have no blank correction applied to the resulting concentrations as reported since all blank extractions performed using the single reaction flask instrument configuration had measurable blank concentrations less than the LLOQ.

With the implementation of the dual reaction flask instrument modifications the LLOQ was able to be adjusted to a lower value and blank corrected results were then able to be included in selected tables as reported.

6. Analyte Description

a. Perfluorooctanoic acid (PFOA)

Perfluorooctanoic acid (PFOA), also known as C8 and perfluorooctanoate, is a synthetic, stable perfluorinated carboxylic acid and fluorosurfactant. One industrial application is as a surfactant in the emulsion polymerization of fluoropolymers. Generally accepted methods for the quantification of PFOA are based on high pressure liquid chromatography (HPLC) and triple stage mass spectrometry. This combination of instrumentation is also known as LC-MS/MS. These combined techniques are well recognized tools for measuring various fluorochemicals including but not limited to: perfluorooctanoic acid (PFOA) perfluorobutanoic acid (C4 acid), perfluorohexanoic acid (C6 acid), perfluorononanoic acid (C9 acid) and perfluorodecanoic acid (C10 acid) at very low concentrations (Olsen *et. al.*, 2007 *EHP* vol. 115, 1298-1305 and Ehresman *et. al.*, *Env Res* vol.103, 176-184).

b. Other perfluorocarboxylic acids (PFCAs)

Other PFCAs identified, quantitated and specifically mentioned in this report include: perfluorobutanoic acid (C4 acid), perfluorohexanoic acid (C6 acid), perfluorononanoic acid (C9 acid) and perfluorodecanoic acid (C10 acid).

D. Test Substance

1. Test Substance 1 – “As Received”

Test Substance 1 is a blended polytetrafluoroethylene (PTFE) powdered matrix as received and initially mixed by Dyneon LLC. It is comprised of equal portions of suspension grade PTFE products as supplied by the contributing FMG member company manufacturers.

2. Test Substance 2 – “Remixed” Test Substance 1

Test Substance 1 was mixed on a rotational mixer for an additional 24 hours by the laboratory performing the actual testing and labeled as Test Substance 2.

3. Cryomilled Test Substance 2

Cryomilled test substance is Test Substance 2 that was cryogenically ground to reduce the particle size. This process is also known as freezer milling, freezer grinding, and cryomilling. It is the act of cooling or chilling a material and then reducing it into a smaller particle size by using repeated physical interactions. When chilled by dry ice, liquid carbon dioxide or liquid nitrogen, thermoplastics can be finely ground to powders suitable for electrostatic spraying and other powder processes. In the cryomilling process, liquid nitrogen chilling and oscillating magnets were used to produce a very fine powder for analysis.

4. ASE Solvent-Washed Test Substance 2

Test Substance 2 was subjected to ASE conditions (minimum 3 cycles of ASE solvent-washing) and then harvested from ASE cells. Multiple cells containing ASE washed Test Substance 2 were pooled to provide adequate amounts of this matrix for further testing.

III. RESULTS OF METHOD DEVELOPMENT EXPERIMENTS

A. Accelerated Solvent Extraction (ASE)

During ASE extractions of PFOA (Larsen *et al.*, *Analyst*, 2005 vol. 130, 59-62.) the test substance is heated to 150°C for 24 hours prior to the initial methanol extraction. The test substance is then extracted using methanol and a Dionex ASE system. The automated system moves a stainless steel cell containing the test substance, and purified sand (Ottawa sand) in between special filter media, into an oven where the temperature is raised to 150°C. Methanol is then introduced into the cell and the cell pressure is raised to 1500 psi. After holding at this temperature and pressure for a set number of minutes, the methanol solvent is collected in 40 mL glass reservoirs. The “Method Development Test Program Guidance Document” specifies multiple extractions to the point where less than 5% of the initially recovered value remains. To date, this has required four complete cycles of preheating and extracting as recommended by Larsen et al.

1. ASE extraction of Test Substance 1 and 2

The primary goal for ASE work was to extract PFOA from the Test Substance exhaustively. The original “As Received” Test substance was referred to as Test Substance 1. Our first goal was to develop a procedure whereby a standard curve could be constructed using blanks and Test Substance 1 samples extracted and quantitated via the ASE.

Fifteen ASE extraction cells were loaded with Ottawa sand and preconditioned with methanol. 10 ng/g PFOA IS (internal standard) was then added to all cells prior to the first elution cycle. Various amounts of PFOA were added to nine of the cells in order to create a standard curve ranging from 0.5 to 17.5 ng/g PFOA. In the next five cells, 2g aliquots of Test Substance 1 were placed in the center of the cells. The final two cells had no standards or samples added to them, and were the ASE blanks. All the cells were placed in an oven for 24 hrs at 150°C. Next the cells were subjected to ASE with methanol as the extraction solvent (Cycle One). The five cells containing Test Substance 1 were again placed in an oven for 24 hrs at 150°C. These five cells were run through ASE a second time using methanol (Cycle Two). These five cells were then placed in an oven for a second 24 hrs at 150°C. Subsequently, the five cells were run through the ASE a third time using methanol (Cycle Three). At the conclusion of this sequence, all collected volumes of methanol (each approximately 19-22 mL) were brought to a final volume of exactly 25 ml by transferring each to a 25 ml volumetric flask and “topping up” with methanol.

An aliquot of 2.5 ml from each volumetric flask was then transferred to a new, clean, disposable polypropylene tube containing 500 μ L of reagent grade H_2O . The methanol was evaporated from the tubes using a LabConco RapidVap, and the residual aqueous phase was then extracted through SPE. The resulting curve had a linear regression equation with an “R” value equal to 0.9992.

The ASE blanks all had measured concentrations less than the LLOQ of 0.5 ng/g. The Cycle One Test Substance 1 samples had recoveries of 1.1, 1.1, and 1.2, 1.0 and 1.2 ng/g PFOA. In both Cycles Two and Three, the recovered amount of PFOA from each of the Test Substance 1 samples was less than the LLOQ (see Table 1). In Table 1, “Absolute Area counts” of the raw data were collected and integrated by the LC-MS/MS instrument software. These data are converted using the instrument calibration curve to ng/g.

Counts that are below the LLOQ level are not converted into ng/g concentrations if they are below the LLOQ for this instrument curve. The absolute area integrated counts for the 0.5 ng/g standard in this experiment were 452,779 counts. As indicated in Table 1, the integrated absolute area counts during subsequent extraction cycles (Cycles 2 and 3) were all less than the integrated counts for the 0.5 ng/g standard. This indicates that PFOA concentrations during extraction cycles 2 and 3 remain less than the LLOQ of 0.5 ng/g as established for this assay.

TABLE 1: ACCELERATED SOLVENT EXTRACTION				
Test Substance 1 (150 °C)				
Sample	PFOA Conc. (ng/g) ASE Cycle 1	Abs. Area (counts) ASE Cycle 1	Abs. Area (counts) ASE Cycle 2	Abs. Area (counts) ASE Cycle 3
Sample #1	1.1	503,129	155,915	134,445
Sample #2	1.1	600,784	192,553	167,416
Sample #3	1.2	579,599	144,243	161,273
Sample #4	1.0	608,422	168,221	121,464
Sample #5	1.2	601,714	176,021	149,466
- PFOA Concentrations (ng/g) for ASE Cycles 2 & 3 were less than LLOQ of 0.5 ng/g				
- Absolute Area (counts) of 0.5 ng/g Standard: 452,779				

A duplicate experiment had recoveries with nearly the same results (see Table 2a). In this case, a large aliquot of the Test Substance was re-mixed to ensure even distribution of the different PTFE products making up the composite. The original composite was prepared from contributions of standard and modified suspension grades of PTFE acquired from the four companies sponsoring the generation test. The re-mixed Test Substance samples were blended and mixed at one of the company’s laboratories. These “re-mixed Test Substance samples” will be referred to as “Test Substance 2” for the remainder of this report.

TABLE 2: ACCELERATED SOLVENT EXTRACTION**Test Substance 2 (100 °C and 150 °C)****Table 2(a): Accelerated Solvent Extraction at 150 °C**

Sample	PFOA Conc. (ng/g) ASE Cycle 1	Abs. Area (counts) ASE Cycle 1	Abs. Area (counts) ASE Cycle 2	Abs. Area (counts) ASE Cycle 3
Sample #1	1.6	703,097	339,356	348,462
Sample #2	1.5	682,066	718,903*	326,216
Sample #3	1.9	586,733	357,578	355,102
Average	1.7			
- Absolute Area (counts) in 0.5 ng/g Std. = 495,128				
* Suspected contamination in liquid transfer				

Based on this work, the amount of PFOA extracted from the re-mixed Test Substance samples (Test Substance 2) was reduced to instrument background levels after one complete ASE extraction cycle. To ensure that the PFOA concentrations were reduced to background levels, a total of three cycles were run during each ASE experiment.

2. 100°C ASE test

PFOA and its salts, the ammonium salt in particular, are susceptible to thermal degradation. Because of this, it was speculated that the PFOA may not be completely extracted at 150°C using ASE, as this temperature is known to be the onset of thermal degradation for the ammonium salt (APFO) [Larsen, et al 2005 Analyst 130, 59-62.]. To avoid this complication another ASE experiment was conducted with Test Substance 2 under the same ASE conditions as before, but at 100°C instead of at 150°C. The oven temperature between cycles was held at 100°C as well.

Once again, after the first cycle, we recovered 1.1-1.4 ng/g PFOA. After the second and third cycles through the ASE, the PFOA concentrations remained less than the LLOQ (see Table 2b). It appeared running the ASE experiment at 100°C instead of 150°C had little effect on the amount of PFOA that was able to be recovered from Test Substance 2.

Table 2(b): Accelerated Solvent Extraction at 100 °C

Sample	PFOA Conc. (ng/g) ASE Cycle 1	Abs. Area (counts) ASE Cycle 1	Abs. Area (counts) ASE Cycle 2	Abs. Area (counts) ASE Cycle 3
Sample #1	1.1	671,879	357,602	283,464
Sample #2	1.2	714,343	309,400	291,504
Sample #3	1.4	776,682	293,737	259,042
Average	1.2			
- Absolute Area (counts) in 0.5 ng/g Std. = 519,091				
- LLOQ = 0.5 ng/g				
- ASE Blank Concentrations in ASE Cycle 1 all < 0.5 ng/g				

3. ASE solvent-washing of Test Substance 2

The original testing sequence as agreed upon during discussions with EPA prior to the start of this method development work consisted of three steps:

1. ASE extraction of the sample to quantify the "baseline" level of PFOA in the Test Substance.
2. Thermal testing via exposure to high temperature with trapping of any PFOA released.
3. A second ASE extraction of the sample to quantify the level of PFOA in the Test Substance after the thermal test.

The three data points were to be used in a mass balance approach to determine how much, if any, PFOA was released due to degradation of the Test Substance sample during the thermal test.

It was decided that Test Substance 2 should be "ASE solvent-washed" prior to thermal testing to remove PFOA residual material. ASE solvent-washing was expected to reduce the uncertainty in the overall test, since we were finding measurable concentrations of PFOA near the LLOQ. It was also expected to help differentiate between PFOA released from the surface of the Test Substance 2 particles, versus release from the interior of the primary particle or potential degradation of Test Substance 2 during the thermal test cycle. The reason that this test would differentiate between PFOA on or near the surface or in the interior of the particles of Test Substance 2 is that the ASE solvent wets the surface well, but does not penetrate into the particle. Test Substance 2 is not soluble or swellable by the ASE solvent (methanol) or by any other commonly used solvent.

ASE-solvent washing was carried out by subjecting Test Substance 2 to three ASE full cycles as described above in section III.A.1. About 30g of Test Substance 2 was ASE solvent-washed and set aside for use in future thermal test experiments.

B. Thermal Test Apparatus

The thermal test is the basis of the overall method being developed. The thermal test conditions being used in our method development work are as follows: Heat a sample of the Test Substance at 315°C for 24 hours in a stream of zero grade air humidified to 50% RH (at RT), and trap PFOA exiting the sample cell in an impinger train. This train consists of two impingers containing high purity water, backed up with an XAD resin cartridge on the end to trap any PFOA that may have migrated through the impingers. The impingers also cool the hot air stream exiting the oven in which the sample reaction flask is held. The sample reaction flask is a small conical flask whose interior is coated with a siloxane coating to minimize adsorption of PFOA onto the walls of the flask and the tubing exiting the flask. See Figure 1 for a view of the sample reaction flask, and Figure 2 for a view of the impinger train.

Figure 1.

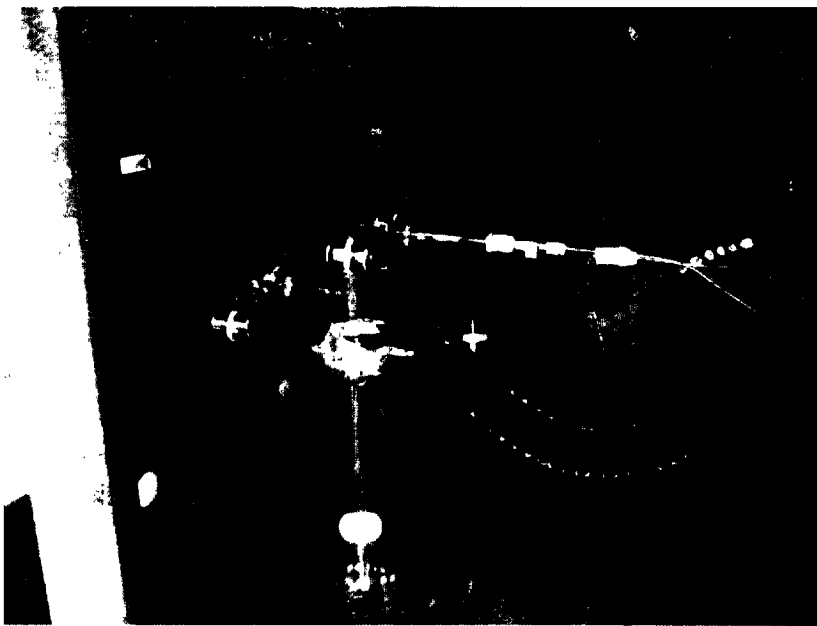
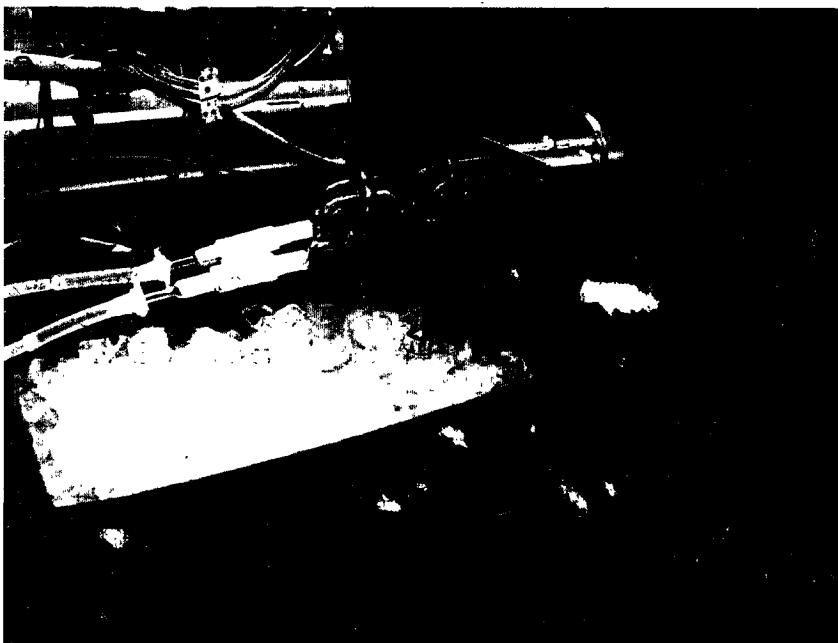


Figure 2.



1. Single Reaction Flask Testing

a. Steps to Optimize Test Apparatus

Over the course of the past year, the conditions have been optimized for thermal test method development work to the point that there is confidence that the results are consistently showing how much PFOA (perfluorooctanoic acid) is being transferred from the

sample cell to the impinger train. The first step in optimizing this system was to determine what background levels of PFOA were present in the system itself. These PFOA background levels may have been introduced into the thermal test system from air in the room in which it is located since low-level quantitative analysis for PFOA is commonly performed in the same lab. Over the course of eight months, nine separate “blank runs” were conducted to determine the system’s background PFOA. These blank runs were normally conducted before or after other experiments where actual testing of PFOA transfer occurred. The temperature cycle used with the thermal test system was always 315°C for 24 hours. In all nine of these blank runs, no single impinger or XAD resin concentration of PFOA exceeded the LLOQ of 0.5 ng/g (see Table 3). Therefore, all blank runs completed were considered to be < 0.5 ng/g. Based on the nine blank runs, our routine background PFOA levels should be less than 0.5 ng/g.

TABLE 3: THERMAL TEST APPARATUS (SINGLE REACTION FLASK)
Blank Runs Under Standard Conditions for 24 hours

Experiment	Conc. (ng/g) in Impinger #1	Conc. (ng/g) in Impinger #2	Conc. (ng/g) in XAD Resin	Conc. (ng/g) in Rxn Flask	Total Conc. (ng/g)
Blank Run #1	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Blank Run #2	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Blank Run #3	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Blank Run #4	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Blank Run #5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Blank Run #6	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Blank Run #7	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Blank Run #8	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Blank Run #9	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
- LLOQ = 0.5 ng/g					

b. Evaluation of PFOA Standard Curve Recovery

We were able to introduce a PFOA standard into the sample flask and move it to the impinger train where it was collected and quantified. The standards were placed in the sample flask located in the oven. The oven was then heated to 315°C and held there for 24 hours. The impinger train was located in an ice bath and had an XAD resin cartridge placed on the end to trap and collect any PFOA that may have migrated through the impingers. This impinger train setup was very efficient at collecting PFOA that was introduced into the sample flask. Five concentrations of PFOA were introduced, including 1.0, 2.5, 5.0, 7.5 and 10 ng/g. Total recovery of these standards in the impinger train setup was between 60-92%, with an overall average recovery of approximately 79%. A curve was plotted of these standards, which had an R^2 value of 0.9929 (see Table 4 & Figure 3). Based on this regression analysis we moved forward testing Test Substance samples.

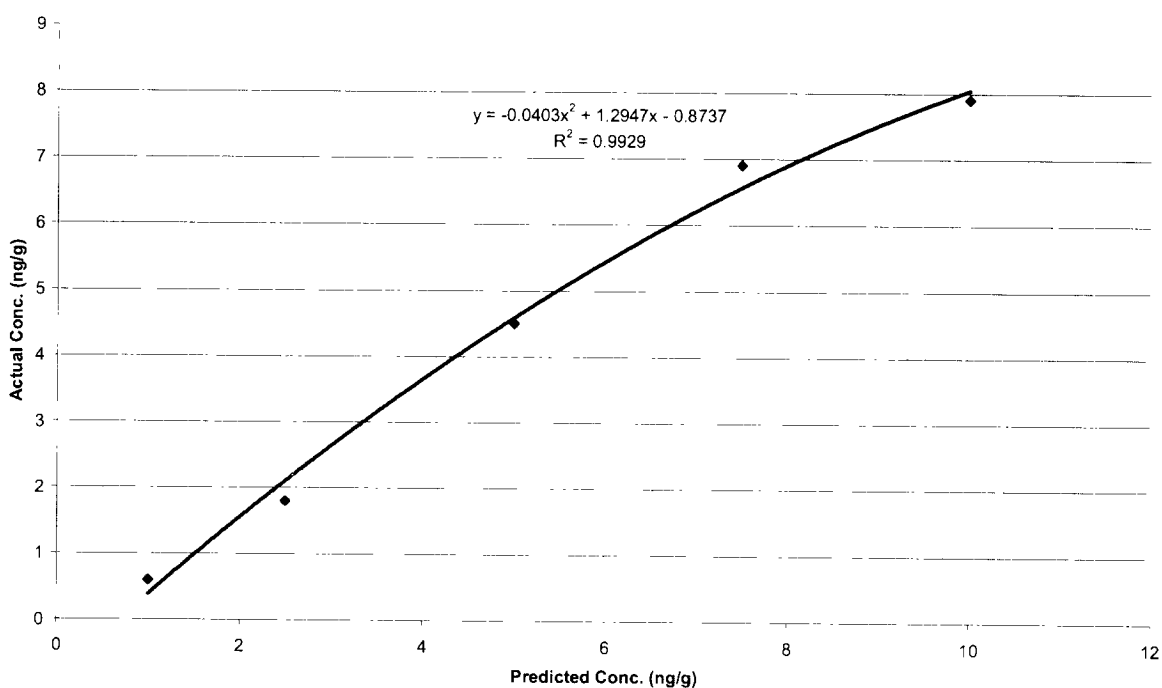
TABLE 4: THERMAL TEST APPARATUS (SINGLE REACTION FLASK)
Standard Conditions with PFOA to Evaluate Standard Curve Recovery

Predicted Std. Conc. (ng/g)	Conc. (ng/g) in impinger #1	Conc.(ng/g) in impinger #2	Conc. (ng/g) in XAD resin	Conc. (ng/g) in Rxn vessel	Total Conc. (ng/g)	Percent Recovery
1	0.6	< 0.5	< 0.5	< 0.5	0.6	60
2.5	1.2	0.6	< 0.5	< 0.5	1.8	72
5	2.6	1.3	0.6	< 0.5	4.5	90
7.5	4.5	1.8	0.6	< 0.5	6.9	92
10	6.3	1.6	< 0.5	< 0.5	7.9	79

- LLOQ = 0.5 ng/g

Figure 3.

**Actual vs. Predicted Conc. Of PFOA Standards
Recovered from Thermal Test Apparatus @ 315°C**



c. Results after Manipulation of Test Substance 2

(1) Thermal Test Experiments of Test Substance 2 and ASE Solvent-Washed Test Substance 2

The first thermal test experiments after efficient transfer of PFOA from the reaction flask to the impinger train as described above were conducted with Test Substance 2 under the standard conditions of 315°C, and 24 hours of constant 50% RH 100 ml/min airflow. The average amount of PFOA that collected from these samples was 9.6 ng/g (see Table 5).

Since the blank runs were consistently at or under the LLOQ, they were not subtracted from the average total concentration.

TABLE 5: THERMAL TEST APPARATUS (SINGLE REACTION FLASK) Standard Conditions for 24 hours with Test Substance 2				
Experiment	Conc. (ng/g) in Impingers*	Conc. (ng/g) in XAD Resin	Conc. (ng/g) in Rxn Flask	Total Conc. (ng/g)
Sample #5	7.1	1.4	< 0.5	8.5
Sample #6	8.9	1.7	< 0.5	10.6
	Average			9.6
- LLOQ = 0.5 ng/g * The contents of Impinger #2 were added to Impinger #1, which was then extracted in a single step using SPE.				

The next series of thermal test experiments were conducted using ASE-solvent washed Test Substance 2 in the reaction flask, again under standard conditions. The average amount of PFOA that was recovered in these runs was 1.4 ng/g (see Table 6). This was a decrease in PFOA concentration compared to the amount (9.6 ng/g) that was transferred from the non-ASE solvent-washed Test Substance 2 (Table 5).

TABLE 6: THERMAL TEST APPARATUS (SINGLE REACTION FLASK)					
Standard Conditions for 24 hours after first subjecting Test Substance 2 to Accelerated Solvent Extraction					
Experiment	Conc. (ng/g) in Impinger #1	Conc. (ng/g) in Impinger #2	Conc. (ng/g) in XAD resin	Conc. (ng/g) in Rxn flask	Total Conc. (ng/g)
Sample #1	0.7	< 0.5	0.9	< 0.5	1.6
Sample #2	0.9	*Added to #1	0.7	< 0.5	1.6
Sample #3	1.9	*Added to #1	0.8	< 0.5	**2.7
Sample #4	0.9	*Added to #1	< 0.5	< 0.5	0.9
Average					1.4
* The contents of Impinger #2 were added to Impinger #1, which was then extracted in a single step using SPE.					
** Suspected contamination in liquid transfer					
- LLOQ = 0.5 ng/g					

(2) **Washing with methanol, acetonitrile and 1.0N Formic Acid**

ASE extraction of Test Substance 2 resulted in the recovery of roughly 1 ng/g of PFOA, but seemed to reduce the amount subsequently recoverable by thermal test treatment by nearly 80% (1.4 ng/g versus 9.6 ng/g, see Tables 5 and 6). Since the result of these two sets of experiments was markedly different, more tests were conducted on Test Substance 2, in an attempt to account for more of the PFOA not recovered by ASE. The first experiment was to extract Test Substance 2 in methanol at room temperature for 24 hours; the amount of PFOA that was extracted in this fashion was less than the LLOQ.

The second test consisted of extracting Test Substance 2 in a 10:1 combination of acetonitrile and 1N formic acid. After shaking the contents for 24 hours, the amount of PFOA that was extracted was also below the LLOQ.

(3) Cryogenic milling

Since the extraction solvent wets but does not dissolve Test Substance 2, there was a possibility that PFOA was physically trapped within the Test Substance 2 particles, where the solvent could not access it. Cryogrinding Test Substance 2 was thought to make the PFOA more accessible by increasing the surface area of the particles. A large aliquot of Test Substance 2 was finely ground using a liquid nitrogen mill. This cryomilled Test Substance 2 was shaken in methanol for 24 hours at room temperature; the results were promising, as 0.9 ng/g of PFOA was extracted, compared to less than the LLOQ for the non-cryomilled Test Substance 2 extracted by the same method, shaking in methanol. This showed that some of the PFOA was protected from solvent extraction by physical trapping within the polymer particles.

Several thermal tests were then conducted on this cryomilled Test Substance 2 under the standard thermal test conditions. Based on three runs, the average amount of PFOA collected from cryomilled Test Substance 2 was 9.0 ng/g (see Table 7). These PFOA concentrations were similar to the test results from the non-cryomilled Test Substance 2 samples, 9.0 ng/g vs. 9.6 ng/g (see Table 5).

TABLE 7: THERMAL TEST APPARATUS (SINGLE REACTION FLASK) Standard Conditions for 24 hours with Cryomilled Test Substance 2				
Sample	Conc. (ng/g) in Impingers*	Conc. (ng/g) in XAD Resin	Conc. (ng/g) in Rxn Vessel	Total Conc. (ng/g)
Sample #8	6.5	1.2	< 0.5	7.7
Sample #9	7.8	2.1	< 0.5	9.9
Sample #10	8.1	1.4	< 0.5	9.5
Average				9.0
* The contents of Impinger #2 were added to Impinger #1, which was then extracted in a single step using SPE. - LLOQ = 0.5 ng/g				

(4) Vacuum Oven Results For Cryomilled Test Substance 2

ASE extraction of the cryomilled Test Substance 2 was ruled out due to concerns that the finely ground material would cause excessive ASE system back pressure. Therefore, the cryomilled Test Substance 2 was placed in a vacuum oven in an attempt to remove PFOA. After heating to approximately 240°C in the vacuum oven for 24 hours, cryomilled Test Substance 2 was subjected to the thermal test cycle under standard conditions. This first experiment resulted in a noticeable decrease in recovered PFOA from approximately 9.0 ng/g to 5.0 ng/g of PFOA (see Table 8a). However, vacuum treatment under these conditions did not remove all of the PFOA contained in Test Substance 2. In a second experiment, the cryomilled Test Substance 2 was heated to 240°C in the vacuum oven for 72 hours, and then

run through the thermal test under standard conditions. In this case, 1.7 ng/g of PFOA was recovered from the impinger train (see Table 8b). In a third experiment, non-cryomilled Test Substance 2 was heated to 240°C in a vacuum oven for 72 hours, and then run through the thermal test under standard conditions, and this sample recovered 1.6 ng/g of PFOA (see Table 8c). When compared to the cryomilled Test Substance 2 at 1.7 ng/g, no significant difference was noted.

TABLE 8: THERMAL TEST APPARATUS (SINGLE REACTION FLASK) Standard Conditions for 24 hours after first subjecting Test Substance 2 to Vacuum Oven Extraction (240 °C)				
Table 8(a): Cryomilled Test Substance 2 After Vacuum Oven Extraction for 24 hours				
Sample	Conc. (ng/g) in Impingers*	Conc. (ng/g) in XAD Resin	Conc. (ng/g) in Rxn Vessel	Total Conc. (ng/g)
Sample #11	4.2	0.8	< 0.5	5.0
Table 8(b): Cryomilled Test Substance 2 After Vacuum Oven Extraction for 72 hours				
Sample	Conc. (ng/g) in Impingers*	Conc. (ng/g) in XAD Resin	Conc. (ng/g) in Rxn Vessel	Total Conc. (ng/g)
Sample #12	1.7	< 0.5	< 0.5	1.7
Table 8(c): Test Substance 2 (Non-cryomilled) After Vacuum Oven Extraction for 72 hours				
Sample	Conc. (ng/g) in Impingers*	Conc. (ng/g) in XAD Resin	Conc. (ng/g) in Rxn Vessel	Total Conc. (ng/g)
Sample #13	1.6	< 0.5	< 0.5	1.6
* The contents of Impinger #2 were added to Impinger #1, which was then extracted in a single step using SPE. - LLOQ = 0.5 ng/g				

Cryomilling Test Substance 2 to reduce the particle size and increase surface area had no significant effect on increasing the recovery of PFOA from the particles using a simple methanol extraction. Cryomilling and heating under vacuum for 72 hours at 240°C did reduce the amount of PFOA recovered by subsequent thermal testing by approximately 80%. Though this cleaning method was designed to reduce the amount of PFOA in Test Substance 2, measurable amounts of PFOA were still recovered by the subsequent thermal test.

d. Results for Thermal Test Periods Exceeding 24 hours

Due to the results of the vacuum oven experiments in which measurable amounts of PFOA were released from heat treating Test Substance 2 after vacuum treatment for up to 72 hours, the thermal test was extended for a longer period of time to see if a point could be reached where no measurable amount of PFOA remained in Test Substance 2. Test Substance 2 was then subjected to a thermal test in which the time was extended from 24 to 56 hours. During this extended thermal test, the impingers and XAD resin were replaced with a new set after time intervals of 4, 8, 32 and 56 hours. The results indicated that most of the PFOA was recovered after 4 hours (5.4 ng/g). However, there were still quantifiable levels of PFOA recovered at up to 56 hours (1.7 ng/g) (see Table 9).

TABLE 9: THERMAL TEST APPARATUS (SINGLE REACTION FLASK)
Standard Conditions for 56 hours with Test Substance 2

Time (hours)	Conc. (ng/g) in Impinger #1	Conc. (ng/g) in Impinger #2	Conc. (ng/g) in XAD Resin	Conc. (ng/g) in Rxn Vessel	Total Conc. (ng/g)
4	3.5	1.1	0.8	N/A	5.4
8	< 0.5	< 0.5	< 0.5	N/A	< 0.5
32	0.7	< 0.5	< 0.5	N/A	0.7
56	1.7	< 0.5	< 0.5	< 0.5	1.7
Total Recovery					7.8
- LLOQ = 0.5 ng/g - Impinger train was replaced after each time interval with a freshly silanized set					

Due to the differences observed in the recovery of PFOA between ASE and thermal testing, it was decided to run a series of ASE extractions on various samples that had been treated in different fashions to see if more PFOA could be recovered by ASE. Each ASE experiment that had been run on non-manipulated Test Substance 2 samples resulted in between 1.0-1.9 ng/g PFOA being recovered after the first cycle. Thereafter, no quantifiable levels above the LLOQ of PFOA were recovered during the second and third ASE cycles (See Tables 1 and 2). The extended thermal test (described in the previous section) resulted in approximately 7.8 ng/g of PFOA being recovered. The series of ASE extractions proposed were:

1. ASE of Test Substance 2, to serve as a control
2. Thermal test of ASE solvent-washed Test Substance 2, then ASE again
3. Thermal test of Test Substance 2, then ASE extracted
4. ASE-solvent washed Test Substance 2, then ASE extracted again

Series 2, re-running ASE on ASE solvent-washed Test Substance 2 stored at room temperature, was done to see if any PFOA in the particle interior diffused over time to the surface and could be recovered. The results showed that the amount of PFOA recovered by ASE extraction remained below the LLOQ in every experiment in this series (see Table 10 below). The ASE solvent-washed Test Substance 2 had about 0.9 ng/g, which was in line with earlier results (see Tables 2a & 2b above).

TABLE 10: ACCELERATED SOLVENT EXTRACTION				
Series 1-4				
Sample	PFOA Conc. (ng/g) in ASE Cycle 1	Abs. Area (counts) in ASE Cycle 1	Abs. Area (counts) in ASE Cycle 2	Abs. Area (counts) in ASE Cycle 3
TABLE 10(a): Series 1: Test Substance 2 subjected once to Accelerated Solvent Extraction				
Sample #1	1.0	262,031	76,475	62,687
Sample #2	0.8	292,692	85,189	74,605
Sample #3	0.8	415,115	240,333	208,506
Sample #4	1.0	450,502	252,647	251,890
Average	0.9			
TABLE 10(b): Series 2: Test Substance 2 subjected twice to Accelerated Solvent Extraction, once before and once after Thermal Test (Single Reaction Flask with Standard Conditions for 24 hours)				
Sample #1	< 0.5	56,669	52,474	37,941
Sample #2	< 0.5	37,504	57,701	38,007
Sample #3	< 0.5	38,445	40,129	40,928
Sample #4	< 0.5	57,988	47,426	50,810
Table 10(c): Series 3: Test Substance 2 subjected once to Accelerated Solvent Extraction after Thermal Test (Single Reaction Flask with Standard Conditions for 24 hours)				
Sample #5	< 0.5	227,534	190,044	195,299
Sample #6	< 0.5	193,145	183,610	203,249
Sample #7	< 0.5	209,458	194,308	190,023
Table 10(d): Series 4: Test Substance 2 subjected twice to Accelerated Solvent Extraction				
Sample #1	< 0.5	85,831	68,634	46,060
Sample #2	< 0.5	86,492	70,686	49,747
Table 10(e): Blanks Subjected twice to Accelerated Solvent Extraction				
Double Blank #1	< 0.5	196,780	281,704	287,503
Double Blank #2	< 0.5	178,144	212,972	184,370
Double Blank #3	< 0.5	242,264	215,432	186,936
- LLOQ = 0.5 ng/g - The above results are from experiments run at different times, so the absolute area counts corresponding to the LLOQ in each experiment differ.				

In a continuation of previous experiments, Test Substance 2 that had not been solvent-washed by ASE was run first through thermal testing, and then run through three ASE cycles (see Table 5 and Table 10c for reference). No measurable levels of PFOA above the LLOQ were detected by ASE (as shown in Table 10c). These samples were then harvested from the ASE cells and run a second time through thermal testing under standard conditions for 24 hours. PFOA concentrations ranging from 0.8-1.1 ng/g of PFOA were recovered from these samples during the second thermal test cycle (see Table 11). The average recovered concentration of PFOA was 0.9 ng/g.

TABLE 11: THERMAL TEST APPARATUS (SINGLE REACTION FLASK) <i>Test Substance 2 subjected to Thermal Testing, then Accelerated Solvent Extraction then a second Thermal Test (Standard Conditions for 24 hours)</i>				
Sample	Conc. (ng/g) in Impingers*	Conc. (ng/g) in XAD Resin	Conc. (ng/g) in Rxn Vessel	Total Conc. (ng/g)
Sample #5	0.8	< 0.5	< 0.5	0.8
Sample #6	0.9	< 0.5	< 0.5	0.9
Sample #7	1.1	< 0.5	< 0.5	1.1
Average				0.9
* The contents of Impinger #2 were added to Impinger #1, which was then extracted in a single step using SPE. - LLOQ = 0.5 ng/g - Results shown are after the second 24 hours of Thermal Testing under Standard Conditions				

e. **Results for PFOA, With Other Homologous Perfluorocarboxylic Acids**

These results led to two questions:

1) Why were low levels of PFOA continuing to be recovered even after 56 hours at 315°C?

2) If PFOA was being released by heating Test Substance 2 at 315°C, were other perfluorocarboxylic acids (PFCAs) being released from Test Substance 2 as well?

The reasoning behind question 2 was that the recovery of PFCAs other than PFOA might help identify the source of the PFOA recovered from Test Substance 2. One potential source of the PFOA in the Test Substance was contamination during manufacturing. Since PFOA is used at manufacturing plants that make the Test Substance constituents, and manufacturing equipment may be shared by different products, cross contamination is possible. If cross contamination by emulsifier grade PFOA occurred, other PFCAs were not expected to be present as contaminants since commercial PFOA does not contain significant concentrations of homologous perfluorocarboxylic acids. After this testing began it was learned that a second potential contamination source is fluorotelomer chemicals, since some fluoropolymer manufacturers also manufacture fluorotelomer products in the same plants.

Therefore, a thermal test was run under standard conditions and tested for the presence of four other perfluorocarboxylic acids: PFBA (perfluorobutanoic acid) PFHxA (perfluorohexanoic acid), PFNA (perfluorononanoic acid) and PFDA (perfluorodecanoic acid) using LC-MS/MS instrumentation. The results showed 7.0 ng/g of PFOA was recovered, similar to our previous findings. In addition, quantifiable amounts of PFHxA (2.1 ng/g), PFNA (3.8 ng/g) and PFDA (3.2 ng/g) were recovered from the impinger train. The amount of PFBA present was less than the LLOQ (see Table 12).

As a result of this thermal test experiment, it was decided that future thermal test experiments would continue to test for the presence of these PFCAs (except PFBA) to see if any trends existed between the concentrations of each of these acids.

TABLE 12: THERMAL TEST APPARATUS (SINGLE REACTION FLASK) Standard Conditions for 24 hours with Test Substance 2				
PFCAs	Conc. in Impingers (ng/g)	Conc. in XAD Resin (ng/g)	Conc. in Rxn Vessel (ng/g)	Total Conc. (ng/g)
PFBA	< 0.5	< 0.5	< 0.5	< 0.5
PFHxA	2.1	< 0.5	< 0.5	2.1
PFOA	6.0	1.0	< 0.5	7.0
PFNA	3.2	0.6	< 0.5	3.8
PFDA	2.6	0.6	< 0.5	3.1
* The contents of Impinger #2 were added to Impinger #1, which was then extracted in a single step using SPE. - LLOQ = 0.5 ng/g				

Testing under wet or dry conditions and in the absence of oxygen was initiated. In all testing up to now, both oxygen and water were present during the thermal test, due to the use of humidified zero air as the carrier gas (as suggested by the EPA).

We first created a “dry” oxygen-free system with approximately 1% RH by exchanging our zero air cylinder for a nitrogen cylinder, and bypassing the humidification chamber. A blank run experiment under 1% RH 100 ml/min dry nitrogen flow for 24 hours at 315°C resulted in the recovery of no quantifiable amounts above the LLOQ (0.5) for PFHxA, PFOA, PFNA and PFDA from the impinger train.

An extended thermal test experiment was conducted, this time under 1% RH 100 ml/min dry nitrogen for 120 hours at 315°C. During this thermal test run, the impingers and XAD resin were replaced with a new set after 24, 48, 72, 96 and 120 hours. PFOA, PFHxA, PFNA, and PFDA were recovered from Test Substance 2; most of it in the first 24 hours (see Table 13a).

We then switched the carrier gas for the thermal test system back to 50% RH zero air and re-tested the same sample used in the dry nitrogen experiment. This was done to see if the 50% RH zero air would cause the release of more PFOA, PFHxA, PFNA and PFDA. This second test was run under standard conditions (50% RH 100 ml/min zero air at 315°C) for 96 hours. During this run, the impingers and XAD resin were again replaced new sets after 24, 48, 72 and 96 hours. The compounds with the highest recoveries were PFOA and PFHxA (see Table 13b). Low levels of PFOA and PFHxA were recoverable from Test Substance 2 even after heating for another 96 hours under zero air at 315°C.

**TABLE 13: THERMAL TEST APPARATUS (SINGLE REACTION FLASK)
Dry Nitrogen Conditions with Test Substance 2 for 120 hours followed
by Standard Conditions (zero air) with same Test Substance 2 Sample
for 96 hours**

Table 13(a): Dry Nitrogen Conditions for 120 hours

Time	Sample Name	PFOA (ng/g)	PFHxA (ng/g)	PFNA (ng/g)	PFDA (ng/g)
24 hr	Impinger #1	3.3	2.4	2.8	1.8
	Impinger #2	0.7	< 0.5	< 0.5	< 0.5
	XAD Resin	< 0.5	< 0.5	< 0.5	< 0.5
Total		4.0	2.4	2.8	1.8
48 hr	Impinger #1	< 0.5	0.5	< 0.5	< 0.5
	Impinger #2	< 0.5	< 0.5	< 0.5	< 0.5
	XAD Resin	< 0.5	< 0.5	< 0.5	< 0.5
Total		< 0.5	0.5	< 0.5	< 0.5
72 hr	Impinger #1	< 0.5	< 0.5	< 0.5	< 0.5
	Impinger #2	< 0.5	< 0.5	< 0.5	< 0.5
	XAD Resin	< 0.5	< 0.5	< 0.5	< 0.5
Total		< 0.5	< 0.5	< 0.5	< 0.5
96 hr	Impinger #1	< 0.5	< 0.5	< 0.5	< 0.5
	Impinger #2	< 0.5	< 0.5	< 0.5	< 0.5
	XAD Resin	< 0.5	< 0.5	< 0.5	< 0.5
Total		< 0.5	< 0.5	< 0.5	< 0.5
120 hr	Impinger #1	< 0.5	< 0.5	< 0.5	< 0.5
	Impinger #2	0.5	< 0.5	< 0.5	< 0.5
	XAD Resin	< 0.5	< 0.5	< 0.5	< 0.5
Total		0.5	< 0.5	< 0.5	< 0.5
Total Recovery (uncorrected)*		4.5	2.9	2.8	1.8
Reaction Flask (after 120 hrs)		< 0.5	< 0.5	< 0.5	< 0.5

- LLOQ = 0.5 ng/g for all compounds

* In a previous blank run under dry nitrogen conditions, background levels of PFOA, PFHxA, PFNA and PFDA were < 0.5 ng/g.

(Table 13 continued on next page)

Table 13(b): Same Test Substance then subjected to Standard Conditions (zero air) for 96 hours					
Time	Sample Name	PFOA (ng/g)	PFHxA (ng/g)	PFNA (ng/g)	PFDA (ng/g)
24 hr	Impinger #1	1.2	1.3	< 0.5	< 0.5
	Impinger #2	0.7	< 0.5	< 0.5	< 0.5
	XAD Resin	< 0.5	< 0.5	< 0.5	< 0.5
	Total	1.9	1.3	< 0.5	< 0.5
48 hr	Impinger #1	< 0.5	1.0	< 0.5	< 0.5
	Impinger #2	< 0.5	< 0.5	< 0.5	< 0.5
	XAD Resin	< 0.5	< 0.5	< 0.5	< 0.5
	Total	< 0.5	1.0	< 0.5	< 0.5
72 hr	Impinger #1	< 0.5	1.4	< 0.5	< 0.5
	Impinger #2	0.6	< 0.5	< 0.5	< 0.5
	XAD Resin	< 0.5	< 0.5	< 0.5	< 0.5
	Total	0.6	1.4	< 0.5	< 0.5
96 hr	Impinger #1	0.7	2.6	< 0.5	< 0.5
	Impinger #2	< 0.5	< 0.5	< 0.5	< 0.5
	XAD Resin	< 0.5	< 0.5	< 0.5	< 0.5
	Total	0.7	2.6	< 0.5	< 0.3
Total Recovery (uncorrected)		3.2	6.3	< 0.5	< 0.5
Reaction Flask (after 96 hrs)		< 0.5	< 0.5	< 0.5	< 0.5
- LLOQ = 0.5 ng/g for all compounds					

Approximately 4.0 ng/g PFOA was recovered in the first 24 hours of dry nitrogen thermal testing (See Table 13a). Subsequent testing of this same sample using zero air and 50% RH released approximately an additional 1.9 ng/g of PFOA in the first 24 hours, and a total of approximately 3.1 ng/g after 96 hours. Measurable amounts of PFOA and PFHxA continued to be recovered even after undergoing extensive heating with dry nitrogen for 120 hours and humidified zero air for 96 hours (see Table 13b above).

Note in Table 13b that lesser amounts of PFOA, PFNA & PFDA were recovered (in total) when we completed thermal testing after first subjecting the Test Substance 2 sample to dry nitrogen instead of just humidified zero air (standard thermal test conditions) during the first 24 hours (compare to Table 12). The total amount of PFHxA recovered actually increased after subjecting the sample to dry nitrogen conditions before running the sample under standard conditions (2.1 ng/g to 6.3 ng/g).

2. Dual Reaction Flask Testing

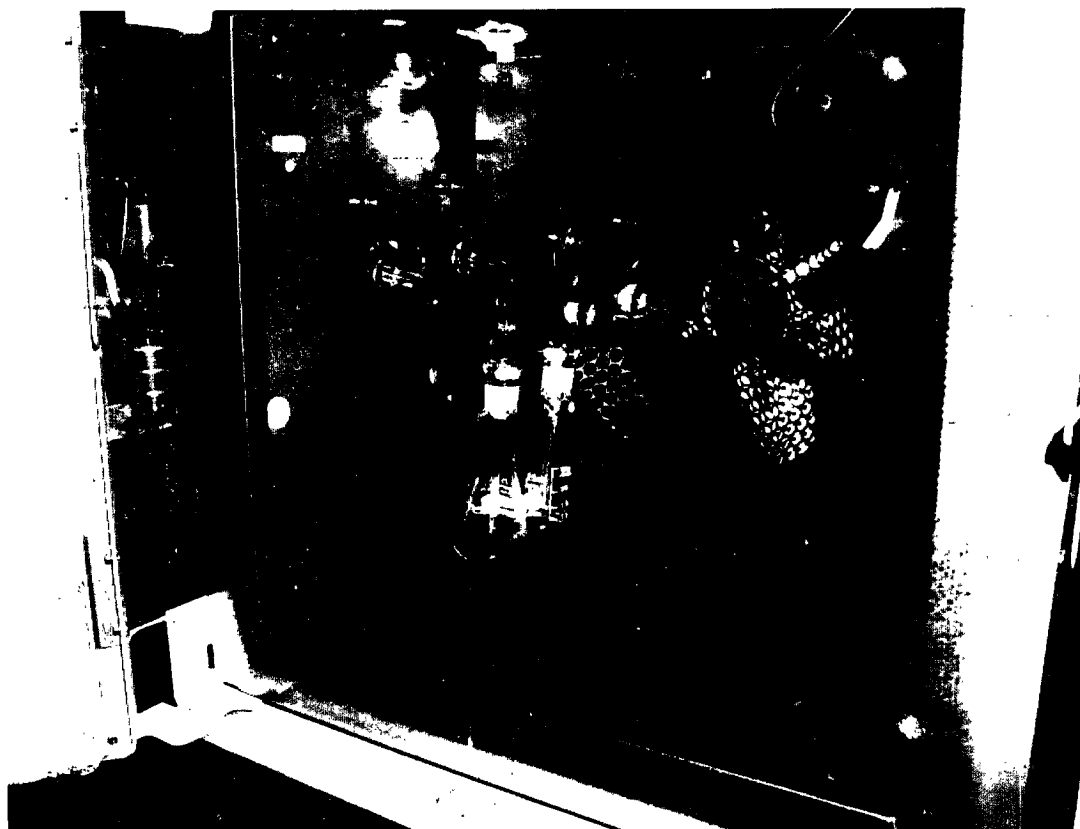
a. Thermal Test Apparatus "Re-design"

All thermal tests are lengthy; many run for several days at a time. Because of this some variability in the values of the system blanks was experienced. An improved blank

testing method was needed to achieve more consistent results, an improved lower limit of quantitation (LLOQ), eliminate the effect of system contamination, and provide “real time” system blanks. These goals were achieved by splitting the heated transfer line in the oven providing airflow to both a sample test system and a blank system. A second impinger train was added to the new line to create an independent blank system.

The amount of airflow through the heated transfer line into the oven was ramped to 200 ml/min, so that both systems would have an equal airflow of 100 ml/min. Each test system, blank and sample, was equipped with its own sample holder, transfer line out of the oven, two impingers and an XAD resin cartridge. These systems were identical in every way. Both were treated with the same process for cleaning and silanization, and both shared a common oven. Both impinger trains were kept in the same ice bath (See Figure 4).

Figure 4.



Before each experiment was conducted, the airflow through each system was equilibrated by gas flow meters placed on the exits. This allowed adjustment to maintain the two systems to the same rate of airflow. Splitting the airflow between a continuous “blank test system” and the “sample test system” allowed the identification of any potential problems with background PFOA contamination in the thermal test. Quantifiable levels of PFOA and the other PFCAs found in the blank test system could be subtracted from that found in the sample test system. A double blank run measured less than 0.5 ng/g of PFOA

for each side of the redesigned test system under the standard conditions for 24 hours. Both sides of the airflow stream measured had comparable concentrations of PFOA. The amounts of PFHxA, PFNA and PFDA measured were less than the LLOQ.

b. Results for PFOA, With Other Homologous Perfluorocarboxylic Acids

Once the redesigned test system was constructed, thermal test experiments commenced to develop and optimize the dual system. All method development work from this point forward was performed using the dual system. The first experiment was conducted using 2g of Test Substance 2 sample. This was placed in the sample holder and heated at standard conditions, a repeat of earlier tests. The amount of PFOA that was found in the experimental sample test system was 5.3 ng/g and the blank test system had a PFOA level below the LLOQ. The concentrations for the other PFCAs were as follows: PFHxA (3.6 ng/g), PFNA (5.0 ng/g) and PFDA (3.3 ng/g) (see Table 14). The blank test system contained less than LLOQ amounts of PFHxA, PFNA and PFDA.

TABLE 14: THERMAL TEST APPARATUS (DUAL REACTION FLASK) Standard Conditions with Test Substance 2					
Flask	Sample Name	PFOA (ng/g)	PFHxA (ng/g)	PFNA (ng/g)	PFDA (ng/g)
Sample Flask	Impinger #1	3.9	3.6	4.3	2.7
	Impinger #2	0.9	< 0.5	0.7	0.6
	XAD Resin	0.5	< 0.5	< 0.5	< 0.5
	Reaction Vessel	< 0.5	< 0.5	< 0.5	< 0.5
Total		5.3	3.6	5.0	3.3
Blank Flask	Impinger #1	< 0.5	< 0.5	< 0.5	< 0.5
	Impinger #2	< 0.5	< 0.5	< 0.5	< 0.5
	XAD Resin	< 0.5	< 0.5	< 0.5	< 0.5
	Reaction Vessel	< 0.5	< 0.5	< 0.5	< 0.5
Total		< 0.5	< 0.5	< 0.5	< 0.5
Corrected Total (Sample - Blank)		5.3	3.6	5.0	3.3
- LLOQ for all compounds = 0.5 ng/mL					

In the next experiment, 2g of Test Substance 2 was held at 315°C for 48 hours under 1% RH (dry) nitrogen. Then the same 2g sample, in the same reaction flask, was held at 315°C for 48 hours under 50% RH zero air. PFOA continued to be recovered in measurable amounts in 50% RH air even after 48 hours in dry nitrogen. The second 24 hours in zero air failed to recover further PFOA (see Table 15).

TABLE 15: THERMAL TEST APPARATUS (DUAL REACTION FLASK)
Dry Nitrogen Conditions for 48 hours with Test Substance 2 followed by Standard Conditions (zero air) with same Test Substance 2 Sample for 48 hours

TABLE 15(a): Test Substance 2 subjected to Dry Nitrogen Conditions for 48 hours

After 24 Hours Dry Nitrogen

Flask	Sample Name	PFOA (ng/g)	PFHxA (ng/g)	PFNA (ng/g)	PFDA (ng/g)
Sample Flask	Impinger #1	4.0	3.9	4.1	2.6
	Impinger #2	< 0.5	< 0.5	< 0.5	< 0.5
	XAD Resin	< 0.5	< 0.5	< 0.5	< 0.5
Total		4.0	3.9	4.1	2.6
Blank Flask	Impinger #1	< 0.5	< 0.5	< 0.5	< 0.5
	Impinger #2	< 0.5	< 0.5	< 0.5	< 0.5
	XAD Resin	< 0.5	< 0.5	< 0.5	< 0.5
Total		< 0.5	< 0.5	< 0.5	< 0.5
Corrected Total (Sample - Blank)		4.0	3.9	4.1	2.6

After Additional 24 Hours Dry Nitrogen

Flask	Sample Name	PFOA (ng/g)	PFHxA (ng/g)	PFNA (ng/g)	PFDA (ng/g)
Sample Flask	Impinger #1	0.8	0.9	0.6	0.5
	Impinger #2	< 0.5	< 0.5	< 0.5	< 0.5
	XAD Resin	< 0.5	< 0.5	< 0.5	< 0.5
Total		0.8	0.9	0.6	0.5
Blank Flask	Impinger #1	< 0.5	< 0.5	< 0.5	< 0.5
	Impinger #2	< 0.5	< 0.5	< 0.5	< 0.5
	XAD Resin	< 0.5	< 0.5	< 0.5	< 0.5
Total		< 0.5	< 0.5	< 0.5	< 0.5
Corrected Total (Sample - Blank)		0.8	0.9	0.6	0.5

(Table 15 continued on next page)

TABLE 15(b): Test Substance 2 subjected to Standard Conditions (zero air) for 48 hours subsequent to 48 hours under dry nitrogen (Table 15(a))					
After 24 Hours Standard Conditions					
Flask	Sample Name	PFOA (ng/g)	PFHxA (ng/g)	PFNA (ng/g)	PFDA (ng/g)
Sample Flask	Impinger #1	1.1	2.2	0.6	0.4
	Impinger #2	0.3	< 0.25	< 0.25	< 0.25
	XAD Resin	1.3	2.6	0.9	0.7
Total		2.7	4.8	1.5	1.1
Blank Flask	Impinger #1	< 0.25	< 0.25	< 0.25	< 0.25
	Impinger #2	< 0.25	< 0.25	< 0.25	< 0.25
	XAD Resin	< 0.25	< 0.25	< 0.25	< 0.25
Total		< 0.25	< 0.25	< 0.25	< 0.25
Corrected Total (Sample - Blank)		2.7	4.8	1.5	1.1
After Additional 24 Hours Standard Conditions					
Flask	Sample Name	PFOA (ng/g)	PFHxA (ng/g)	PFNA (ng/g)	PFDA (ng/g)
Sample Flask	Impinger #1	0.5	0.3	< 0.25	< 0.25
	Impinger #2	< 0.25	< 0.25	< 0.25	< 0.25
	XAD Resin	0.3	0.5	< 0.25	< 0.25
Total		0.8	0.8	< 0.25	< 0.25
Blank Flask	Impinger #1	0.3	< 0.25	< 0.25	< 0.25
	Impinger #2	0.4	< 0.25	< 0.25	< 0.25
	XAD Resin	< 0.25	< 0.25	< 0.25	< 0.25
Total		0.7	< 0.25	< 0.25	< 0.25
Corrected Total (Sample - Blank)		0.1	0.8	< 0.25	< 0.25
- LLOQ for all compounds = 0.5 ng/mL for samples in Table 15a - LLOQ for all compounds = 0.25 ng/mL for samples in Table 15b					

Regarding the PFHxA recoveries, a total of 10.4 ng/g were recovered; this is more than the total amount of PFOA recovered (7.6 ng/g). Most of the PFCAs were trapped during the first 24 hours of heating, regardless of which carrier gas was used (see Table 15).

The conditions of the next experiment were modified slightly. 2g of Test Substance 2 was held for 24 hours at 315°C in 1% RH dry nitrogen. After the first 24 hours under dry nitrogen, the sample was kept in the sample holder at room temperature for 24 hours. This sample was then run under 1% RH dry nitrogen for a second 24 hour period at 315°C. The sample was then held at room temperature for a second 24 hour period. Finally, the sample was held at standard conditions (315°C for 24 hours, 50% RH zero air). Impinger trains were replaced after each 24 hour heating cycle. We were looking for any effects that would occur by resting the sample at room temperature in the middle of an extended heating process. The results of this experiment were not significantly different from previous extended thermal test experiments (see Table 16). Most of the PFCAs were recovered from the sample holder during the first 24 hours of heating using either the nitrogen or the zero air.

It appears that the second and third sets of impingers used in this experiment may have been contaminated with small amounts of PFOA.

After the second 24 hours under dry nitrogen, the recovered amount of all PFCAs is much less than after the first 24 hours. When this sample was exposed to humid air the recoveries of all PFCAs increased significantly compared to the second twenty four hours under nitrogen. The level of recovered PFHxA was higher than the amount of PFOA recovered under these conditions (see Table 16).

TABLE 16: THERMAL TEST APPARATUS (DUAL REACTION FLASK)					
<i>Dry Nitrogen Conditions for 48 hours with Test Substance 2 followed by Standard Conditions (zero air) for 24 hours with same Test Substance 2 Sample</i>					
TABLE 16(a): Test Substance 2 subjected twice to Dry Nitrogen Conditions for 24 hours (with a 24 hour holding period in same capped flask at room temperature in between each 24 hour interval)					
<i>After 24 Hours Dry Nitrogen</i>					
Flask	Sample Name	PFOA (ng/g)	PFHxA (ng/g)	PFNA (ng/g)	PFDA (ng/g)
Sample Flask	Impinger #1	3.2	1.1	3.4	2.6
	Impinger #2	0.7	< 0.25	0.5	0.3
	XAD Resin	0.4	< 0.25	0.4	0.4
Total		4.3	1.1	4.4	3.3
Blank Flask	Impinger #1	0.4	< 0.25	< 0.25	< 0.25
	Impinger #2	0.2	< 0.25	< 0.25	< 0.25
	XAD Resin	< 0.1	< 0.25	< 0.25	< 0.25
Total		0.6	< 0.25	< 0.25	< 0.25
Corrected Total (Sample - Blank)		3.7	1.1	4.3	3.3
<i>After Additional 24 Hours Dry Nitrogen</i>					
Flask	Sample Name	PFOA (ng/g)	PFHxA (ng/g)	PFNA (ng/g)	PFDA (ng/g)
Sample Flask	Impinger #1	1.0	0.4	0.6	0.6
	Impinger #2	0.3	< 0.25	< 0.25	< 0.25
	XAD Resin	0.2	< 0.25	< 0.25	< 0.25
Total		1.5	0.4	0.6	0.6
Blank Flask	Impinger #1	0.4	< 0.25	< 0.25	< 0.25
	Impinger #2	0.7	< 0.25	< 0.25	< 0.25
	XAD Resin	0.3	< 0.25	< 0.25	< 0.25
Total		1.3	< 0.25	< 0.25	< 0.25
Corrected Total (Sample - Blank)		0.2	0.4	0.6	0.6

(Table 16 continued on next page)

TABLE 16(b): Test Substance 2 subjected once to Standard Conditions (zero air) for 24 hours after 48 hours under dry nitrogen (Table 16(a))

Flask	Sample Name	PFOA (ng/g)	PFHxA (ng/g)	PFNA (ng/g)	PFDA (ng/g)
Sample Flask	Impinger #1	5.0	9.7	4.0	3.4
	Impinger #2	2.0	0.8	0.3	< 0.25
	XAD Resin	1.1	0.8	0.3	0.3
Total		8.1	11.3	4.6	3.7
Blank Flask	Impinger #1	0.5	< 0.25	< 0.25	< 0.25
	Impinger #2	1.9	< 0.25	< 0.25	< 0.25
	XAD Resin	0.8	< 0.25	< 0.25	< 0.25
Total		3.2	< 0.25	< 0.25	< 0.25
Corrected Total (Sample - Blank)		4.9	11.3	4.6	3.7
- LLOQ for PFOA = 0.1 ng/mL for all samples - LLOQ for PFHxA, PFNA & PFDA = 0.25 ng/mL for all samples					

Similar amounts of all of the PFCAs were recovered using 50% RH and zero air regardless of resting the test material between heating cycles under dry nitrogen conditions. The similar amounts for all PFCAs recovered were observed after: 1) heating with nitrogen for 24 hours at 315°C, resting for 24 hours at room temperature and heating again for 24 hours with nitrogen, or 2) uninterrupted heating for 48 hours using dry nitrogen. Due to the lengthy nature of these experiments, it was decided not to repeat these tests a second time.

The next set of experiments involved using dry nitrogen for 24 hours followed by a second and third 24 hour period with humidified nitrogen (See Table 17). Comparing these wet nitrogen results to the results discussed above and detailed in Table 16, a significant difference was noted. When the sample was exposed to humidified zero air after exposure to dry nitrogen (N₂), more PFOA and the other PFCAs were recovered from the test system than were recovered when using humidified nitrogen. Based on these experimental results it would appear that more PFCAs are recovered when oxygen (O₂) is present in the air stream. (Compare Table 16 to Table 17).

TABLE 17: THERMAL TEST APPARATUS (DUAL REACTION FLASK)					
Test Substance 2 subjected to Dry Nitrogen Conditions for 24 hours followed by Wet Nitrogen Conditions for 48 hours with same Test Substance 2 Sample					
TABLE 17(a): Test Substance Subjected to Dry Nitrogen Conditions for 24 Hours					
Flask	Sample Name	PFOA (ng/g)	PFHxA (ng/g)	PFNA (ng/g)	PFDA (ng/g)
Sample Flask	Impinger #1	2.8	1.5	2.2	1.6
	Impinger #2	0.9	0.3	0.7	0.5
	XAD Resin	0.3	0.1	0.2	0.2
Total		4.0	1.9	3.1	2.3
Blank Flask	Impinger #1	0.1	< 0.1	< 0.1	< 0.1
	Impinger #2	0.1	< 0.1	< 0.1	< 0.1
	XAD Resin	0.2	< 0.1	< 0.1	< 0.1
Total		0.4	< 0.1	< 0.1	< 0.1
Corrected Total (Test – Blank)		3.6	1.9	3.1	2.3
TABLE 17(b): Test Substance Then Subjected to Wet Nitrogen Conditions for 48 Hours					
After 24 Hours Wet Nitrogen					
Flask	Sample Name	PFOA (ng/g)	PFHxA (ng/g)	PFNA (ng/g)	PFDA (ng/g)
Sample Flask	Impinger #1	0.7	0.4	0.5	0.5
	Impinger #2	0.2	< 0.1	< 0.1	< 0.1
	XAD Resin	0.2	< 0.1	< 0.1	< 0.1
Total		1.1	0.4	0.5	0.5
Blank Flask	Impinger #1	0.1	< 0.1	< 0.1	< 0.1
	Impinger #2	0.2	< 0.1	< 0.1	< 0.1
	XAD Resin	0.1	< 0.1	< 0.1	< 0.1
Total		0.4	< 0.1	< 0.1	< 0.1
Corrected Total (Test – Blank)		0.7	0.4	0.5	0.5
After Additional 24 Hours Wet Nitrogen					
Flask	Sample Name	PFOA (ng/g)	PFHxA (ng/g)	PFNA (ng/g)	PFDA (ng/g)
Sample Flask	Impinger #1	0.4	0.2	0.3	0.3
	Impinger #2	0.2	< 0.1	0.1	0.2
	XAD Resin	0.2	< 0.1	< 0.1	< 0.1
Total		0.8	0.2	0.4	0.5
Blank Flask	Impinger #1	NQ	< 0.1	< 0.1	< 0.1
	Impinger #2	0.1	< 0.1	< 0.1	< 0.1
	XAD Resin	0.1	< 0.1	< 0.1	< 0.1
Total		0.2	< 0.1	< 0.1	< 0.1
Corrected Total (Test – Blank)		0.6	0.2	0.4	0.4
OVERALL TOTAL		4.9	2.5	4.0	3.2
- LLOQ = 0.1 ng/g for all compounds - In this experiment, only one sample flask and one blank flask were used - Impingers & XAD resins were changed between each 24-hour period - While switching from dry nitrogen to wet nitrogen, oven temperature was maintained at 315 °C					

Experiments were designed to find the optimal temperature for PFCA recovery from Test Substance 2 during the thermal test. At 100°C, 2g of Test Substance 2 was run under 100 ml/min 50% relative humidity airflow for 24 hrs. The same 2g sample was run sequentially at 150°C for 24 hrs, at 200°C for 24 hrs, at 250°C for 24 hrs and finally at 300°C for 24 hours. In this experiment, only one sample holder and one blank sample holder were used. Impingers and XAD resins were changed between each temperature level. Between temperature levels, the oven was ballistically ramped to the next temperature. It was noted that an increase in concentrations of each of the compounds were recovered when temperatures exceeded 250°C with the maximum occurring at 300°C (see Table 18).

TABLE 18: THERMAL TEST APPARATUS (DUAL REACTION FLASK) <i>Sequence of Variable Temperature Conditions (under zero air) for 24-hour intervals on same Test Substance 2 Sample</i>					
Table 18(a): After 24 Hours at 100 °C					
Flask	Sample Name	PFOA (ng/g)	PFHxA (ng/g)	PFNA (ng/g)	PFDA (ng/g)
Sample Flask	Impinger #1	0.7	< 0.1	< 0.1	< 0.1
	Impinger #2	0.1	< 0.1	< 0.1	< 0.1
	XAD Resin	0.1	< 0.1	< 0.1	< 0.1
	Total	0.9	< 0.1	< 0.1	< 0.1
Blank Flask	Impinger #1	0.1	< 0.1	< 0.1	< 0.1
	Impinger #2	0.2	< 0.1	< 0.1	< 0.1
	XAD Resin	0.1	< 0.1	< 0.1	< 0.1
	Total	0.4	< 0.1	< 0.1	< 0.1
Corrected Total (Test - Blank)		0.5	< 0.1	< 0.1	< 0.1
Table 18(b): Same Sample After Additional 24 Hours at 150 °C					
Flask	Sample Name	PFOA (ng/g)	PFHxA (ng/g)	PFNA (ng/g)	PFDA (ng/g)
Sample Flask	Impinger #1	0.3	< 0.1	0.1	0.2
	Impinger #2	0.1	< 0.1	< 0.1	< 0.1
	XAD Resin	0.1	< 0.1	< 0.1	< 0.1
	Total	0.5	< 0.1	0.1	0.2
Blank Flask	Impinger #1	< 0.1	< 0.1	< 0.1	< 0.1
	Impinger #2	< 0.1	< 0.1	< 0.1	< 0.1
	XAD Resin	< 0.1	< 0.1	< 0.1	< 0.1
	Total	< 0.1	< 0.1	< 0.1	< 0.1
Corrected Total (Test - Blank)		0.5	< 0.1	0.1	0.2

(Table 18 continued on next page)

Table 18(c): Same Sample After Additional 24 Hours at 200°C					
Flask	Sample Name	PFOA (ng/g)	PFHxA (ng/g)	PFNA (ng/g)	PFDA (ng/g)
Sample Flask	Impinger #1	0.6	0.3	0.8	0.7
	Impinger #2	< 0.1	< 0.1	< 0.1	< 0.1
	XAD Resin	< 0.1	< 0.1	< 0.1	< 0.1
	Total	0.6	0.3	0.8	0.7
Blank Flask	Impinger #1	< 0.1	< 0.1	< 0.1	< 0.1
	Impinger #2	< 0.1	< 0.1	< 0.1	< 0.1
	XAD Resin	< 0.1	< 0.1	< 0.1	< 0.1
	Total	< 0.1	< 0.1	< 0.1	< 0.1
Corrected Total (Test - Blank)		0.6	0.3	0.8	0.7
Table 18(d): Same Sample After Additional 24 Hours at 250 °C					
Flask	Sample Name	PFOA (ng/g)	PFHxA (ng/g)	PFNA (ng/g)	PFDA (ng/g)
Sample Flask	Impinger #1	1.4	0.8	2.0	1.6
	Impinger #2	< 0.1	< 0.1	< 0.1	< 0.1
	XAD Resin	0.2	< 0.1	0.1	0.2
	Total	1.6	0.8	2.1	1.8
Blank Flask	Impinger #1	< 0.1	< 0.1	< 0.1	< 0.1
	Impinger #2	< 0.1	< 0.1	< 0.1	< 0.1
	XAD Resin	< 0.1	< 0.1	< 0.1	< 0.1
	Total	< 0.1	< 0.1	< 0.1	< 0.1
Corrected Total (Test - Blank)		1.6	0.8	2.1	1.8
Table 18(e): Same Sample After Additional 24 Hours at 300 °C					
Flask	Sample Name	PFOA (ng/g)	PFHxA (ng/g)	PFNA (ng/g)	PFDA (ng/g)
Sample Flask	Impinger #1	2.1	1.3	1.8	1.9
	Impinger #2	0.2	0.4	0.1	< 0.1
	XAD Resin	0.9	1.3	0.7	0.7
	Total	3.2	3.0	2.6	2.6
Blank Flask	Impinger #1	< 0.1	< 0.1	< 0.1	< 0.1
	Impinger #2	< 0.1	< 0.1	< 0.1	< 0.1
	XAD Resin	< 0.1	< 0.1	< 0.1	< 0.1
	Total	< 0.1	< 0.1	< 0.1	< 0.1
Corrected Total (Test - Blank)		3.2	3.0	2.6	2.6
Cumulative Total		6.4	4.1	5.6	5.3
- LLOQ = 0.1 ng/g for all compounds - Impingers & XAD resins were swapped out between each temperature level - Between temperature levels, oven was ballistically ramped to next temperature					

Experiments were run at 225°C, 250°C, 275°C and 315°C to refine the optimal temperature level. Separate thermal test experiments were conducted at each temperature, where 2g of Test Substance 2 was run under 100 ml/min 50% relative humidity airflow for 24 hrs. Table 19 presents the results, which seem to indicate that as the temperature of the

sample is increased, more of each of the PFCAs are recovered from the impinger train up to at least 315°C (see Table 19).

TABLE 19: THERMAL TEST APPARATUS (DUAL REACTION FLASK) Variable Temperature Conditions (under zero air) for 24 hour intervals with different Test Substance 2 Samples					
Table 19(a): After 24 Hours at 225 °C					
Flask	Sample Name	PFOA (ng/g)	PFHxA (ng/g)	PFNA (ng/g)	PFDA (ng/g)
Sample Flask	Impinger #1	1.7	0.5	1.4	0.9
	Impinger #2	0.5	< 0.1	0.2	0.1
	XAD Resin	0.4	< 0.1	0.1	0.1
Total		2.6	0.5	1.7	1.1
Blank Flask	Impinger #1	0.2	< 0.1	< 0.1	< 0.1
	Impinger #2	0.2	< 0.1	< 0.1	< 0.1
	XAD Resin	0.2	< 0.1	< 0.1	< 0.1
Total		0.6	< 0.1	< 0.1	< 0.1
Corrected Total (Test - Blank)		2.0	0.5	1.7	1.1
Table 19(b): After 24 Hours at 250 °C					
Flask	Sample Name	PFOA (ng/g)	PFHxA (ng/g)	PFNA (ng/g)	PFDA (ng/g)
Sample Flask	Impinger #1	2.5	0.8	2.2	1.2
	Impinger #2	0.5	< 0.1	0.3	0.2
	XAD Resin	0.5	< 0.1	0.2	0.1
Total		3.5	0.8	2.7	1.5
Blank Flask	Impinger #1	0.4	< 0.1	< 0.1	< 0.1
	Impinger #2	0.2	< 0.1	< 0.1	< 0.1
	XAD Resin	0.3	< 0.1	< 0.1	< 0.1
Total		0.9	< 0.1	< 0.1	< 0.1
Corrected Total (Test - Blank)		2.6	0.8	2.7	1.5
Table 19(c): After 24 Hours at 275 °C					
Flask	Sample Name	PFOA (ng/g)	PFHxA (ng/g)	PFNA (ng/g)	PFDA (ng/g)
Sample Flask	Impinger #1	2.7	1.1	1.9	1.0
	Impinger #2	1.0	< 0.1	0.7	0.4
	XAD Resin	0.5	0.1	0.3	0.2
Total		4.2	1.2	2.9	1.6
Blank Flask	Impinger #1	0.6	< 0.1	< 0.1	< 0.1
	Impinger #2	0.3	< 0.1	< 0.1	< 0.1
	XAD Resin	0.2	< 0.1	< 0.1	< 0.1
Total		1.1	< 0.1	< 0.1	< 0.1
Corrected Total (Test - Blank)		3.1	1.2	2.9	1.6

(Table 19 continued on next page)

Table 19(d): After 24 Hours at 315 °C (Data from Table 14)				
	PFOA (ng/g)	PFHxA (ng/g)	PFNA(ng/g)	PFDA (ng/g)
Corrected Total (Test - Blank)	5.3	3.6	5.0	3.3
- LLOQ = 0.1 ng/g for all compounds tested except for the 315 °C sample where LLOQ = 0.5 - A different sample flask and blank flask was used at each temperature level - Impingers & XAD resins were swapped between each 24 hr period - The experiment was run under continuous 50% RH zero air				

IV. GLOSSARY OF TERMS AND ABBREVIATIONS

Accelerated Solvent Extraction (ASE) – An automated instrument that uses a combination of high temperature and high pressure solvent in an extraction process. This instrument was designed to increase recovery of selected compounds from semi-solid and/or solid materials.

Ammonium perfluorooctanoate (APFO) – Ammonium perfluorooctanoate is the ammonia salt of perfluorooctanoic acid (PFOA), having the chemical formula $C_7F_{15}CO_2NH_4$. APFO is identified by CAS# 3825-26-1. See also PFOA.

Differential Scanning Calorimetry (DSC) – a thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and a reference mass are measured as a function of temperature. The main application of DSC is in studying phase transitions, such as melting, glass transitions, or exothermic decompositions. These transitions involve energy changes or heat capacity changes that can be detected by DSC with great sensitivity.

Framework Test Program Guidance – a document entitled “Framework for Test Method for Measurement of Perfluorooctanoic Acid Generated from Thermal Degradation of Fluoropolymers.”

Lower Limit of Quantitation (LLOQ) – the lowest amount of an analyte in a sample that can be quantitatively determined with suitable precision and accuracy. The LLOQ of the analytical methods used for PFOA analysis in the PSE and TGT methods is equal to the lowest calibration standard actually used in establish in the actual calibration curve.

Method Development Test Program Guidance – a document entitled “Method Development for Testing Generation of Perfluorooctanoic Acid from Thermal Degradation of Fluoropolymers.”

Modified PTFE – refers (for the purposes of this study) to those grades of polytetrafluoroethylene that are made: 1) by a suspension polymerization process (Drobny, *Technology of Fluoropolymers*), 2) typically without using PFOA, and 3) contain a second comonomer. The comonomers are typically perfluorinated vinyl ethers, and are present in low amounts (~0.1% or less) in the final polymer. Modified PTFE is identified by CAS# 3825-26-1, or by CAS# 26655-00-5.

Part per million (ppm) and parts per billion (ppb): Parts-per notation is used, especially in science and engineering, to denote relative proportions in measured quantities; particularly in low-value (high-ratio) proportions at the parts-per-million (ppm) 10^{-6} and parts-per-billion (ppb) 10^{-9} level. One part in one million equal parts is a part per million, one part in one billion equal parts is a part per billion. 1 nanogram / gram (ppb) of PFOA would be 0.000000001 grams of PFOA in 1.0 grams of material (such as the test substance).

Perfluorooctanoic acid (PFOA) – Perfluorooctanoic acid is a fully fluorinated carboxylic acid, having the chemical formula $C_7F_{15}CO_2H$. PFOA is identified by CAS# 335-67-1. When the term PFOA is used in this Protocol, it is inclusive of both PFOA and APFO. More specifically, the perfluorooctanoate anion is the chemical species detected by the analytical methods used in this study.

Polytetrafluoroethylene (PTFE) – refers, for the purposes of this study, to those grades of polytetrafluoroethylene made by a suspension polymerization (Drobny, *Technology of Fluoropolymers*) processes and typically not using PFOA. PTFE made by this process is also known as “granular PTFE” by the fluoropolymer processing industry. PTFE is identified by CAS# 3825-26-1.

Solid Phase Extraction (SPE) – A technique that is a separation process by which compounds that are dissolved or suspended in a liquid mixture are separated from other compounds in the mixture according to their physical and chemical properties. Analytical laboratories use solid phase extraction to concentrate and purify samples for analysis. Solid phase extraction can be used to isolate analytes of interest from a wide variety of matrices, including urine, blood, water, beverages, soil, and animal tissue. SPE uses the affinity of solutes dissolved or suspended in a liquid (known as the mobile phase) for a solid through which the sample is passed (known as the stationary phase) to separate a mixture into desired and undesired components. The result is that either the desired analytes of interest or undesired impurities in the sample are retained on the stationary phase. The portion that passes through the stationary phase is collected or discarded, depending on whether it contains the desired analytes or undesired impurities. If the portion retained on the stationary phase includes the desired analytes, they can then be removed from the stationary phase for collection in an additional step, in which the stationary phase is rinsed with an appropriate eluent.

Test Sponsors – collectively, AGC Chemicals Americas, Inc.; Daikin America, Inc.; Dyneon LLC; and E.I. du Pont de Nemours and Company.

Test Substance – the industry PTFE composite sample specified in Section II of this Protocol.

Trifluoroacetic acid (TFA) – a strong carboxylic acid with the formula CF_3CO_2H .

Thermal Test – the thermal test is a test conducted using a special-purpose device developed by the Test Sponsors. This test subjects a sample of the Test Substance to a specified temperature under specified conditions for a specified time interval. Clean, moisturized air passes through the device in a controlled and reproducible manner. The outlet air stream is sampled to collect PFOA potentially released from the polymer.

XAD – a highly absorbent ion-exchange resin used in continuous sampling of organic materials, especially for monitoring of pollutants in gas streams. It is used for collecting specific compounds in air because it traps and retains compounds of interest even in the presence of other compounds, doesn't alter the compound of interest, and allows the collected compounds to be readily extracted for analysis.

Zero Grade Air (or Zero Air) – Commercially purchased compressed air that has met standards for hydrocarbon content at less than 0.1 part per million (ppm). Every cylinder of zero grade air is supplied with an individual certificate of analysis to insure the quality required was provided. Zero Grade Air as certified is required to have oxygen content between 20 and 21 percent, less than 5 ppm residual water and less than 1 ppm of the following contaminants: carbon monoxide, carbon dioxide, and sulfur dioxide.

V. REFERENCES

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