



February 26, 2010

CERTIFIED MAIL

Document Processing Center
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,

3M is submitting this notice to supplement previous submissions on sulfonyl and carboxylic-based fluorochemicals (FCs). Over the last several years, the Fluoropolymer Manufacturers Group (FMG), a trade association of which 3M's subsidiary, Dyneon, LLC, is a member,¹ has voluntarily sponsored 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 part of this commitment, 3M has dedicated laboratory space and personnel to construct test equipment and has been performing the experiments using this equipment. 3M, on behalf of the FMG, has submitted two progress reports to date, one in April 2007 and a second in September 2008. FMG and U.S. EPA also have engaged periodically in technical dialogue.

3M is now working with the FMG to prepare the third of these reports. The experiments encompassed by this third report have produced certain data summarized below:

¹ The FMG is organized under the Society of the Plastics Industry, Inc. and has the following member companies: AGC Chemicals Americas, Inc.; Daikin America, Inc.; Dyneon, LLC; and E.I. du Pont de Nemours and Company.

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- ⇒ Samples of the Test Substance² were subjected to three cycles of Accelerated Solvent Extraction (ASE) using methanol as the extraction solvent with a 0.5 ng/g lower limit of quantification (LLOQ). Before each ASE cycle, the samples were heated in an oven for 24 hours at either 100 °C or 150 °C. PFOA was recovered in amounts ranging from 1 to 1.4 ng/g after the first cycle, and not recovered during the second and third cycles. Following ASE, some of these same Test Substance samples were then subjected to various experiments in a test apparatus specially constructed for this Method Development effort. During these experiments, the samples were placed in an oven heated to 315 °C under various conditions (e.g., 50% RH 100 ml/min air flow; 1% RH 100 ml/min dry nitrogen; 1% RH 100 ml/min wet nitrogen; 50% RH zero air) for various time intervals, with the longest interval of any experiment being 120 hours. PFOA was recovered from the test apparatus impingers at all time intervals, although the highest PFOA recoveries consistently occurred after the first 24 hour interval, with lower amounts thereafter. The amounts of PFOA recovered from the test apparatus impingers after the first 24 hour interval consistently exceeded the amounts recovered after the first ASE extraction cycle. Total amounts of PFOA recovered during these experiments after passage of all time intervals were low, ranging from 4.6 to 6.4 ng/g.
- ⇒ Similar experiments also were performed with reference to other perfluorocarboxylic acids (PFCAs), specifically PFHxA, PFNA and PFDA.³ In all cases, the ASE cycles did not recover any of these PFCAs from the Test Substance sample. These PFCAs were recovered, however, from the test apparatus impingers at all time intervals up to 120 hours. As with PFOA, the highest recoveries consistently occurred at the 24 hour interval, with lower amounts thereafter, and total amounts recovered after passage of all time intervals were low, ranging from 2.5 to 11.3 ng/g (PFHxA), below LLOQ to 4.0 ng/g (PFNA) and below LLOQ to 3.2 ng/g (PFDA).
- ⇒ Experiments also were performed using the same test apparatus for a 24 hour period at lower temperatures of 100, 150, 225, 250 and 275 °C. Recovery of PFOA and the other PFCAs occurred at these lower temperatures, although amounts recovered were lower as compared to the experiments at 315 °C.

The FMG has informed the U.S. EPA office with whom it has been in technical dialogue of these results. FMG intends to continue this technical dialogue, and

² The Test Substance is a composite derived from polytetrafluoroethylene (PTFE) samples supplied by those FMG member companies who manufactured PTFE via a suspension polymerization process not using PFOA as a polymerization aid.

³ Initial experiments on other compounds also included PFBA (perfluorobutanoic acid). These experiments indicated that PFBA was not present above the LLOQ, and therefore, it was not included in further experiments.

specifically, to discuss approaches for supplementing these results through further experiments.

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. We will submit the third report now being prepared to the docket as soon as available. In the meantime, we are enclosing the first and second reports already submitted to U.S. EPA, which contain further background information about the Generation Test Method Development Experiments and earlier results.

If you have any questions, please do not hesitate to contact Deanna Luebker at (651) 737-1274 or djluebker@mmm.com.

Sincerely,

A handwritten signature in black ink that reads "Jean B. Sweeney". The signature is written in a cursive, flowing style.

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

Enclosures (2)

3M Corporate Toxicology

Analytical Laboratory Bldg 236

To: George Millet

**From: Jeremy Zitzow
Dave Ehresman
Venkateswarlu Pothapragada**

**Study: Annual Report on
Evaluation of any thermal generation of PFOA from PTFE**

Date: November 13, 2006

Outline

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Detailed Report

3. Experimental – pg. 5-6
 - A. Accelerated Solvent Extraction of PFOA
 - B. Setup of the Equipment for heating samples and transfer and collection of PFOA.
 - C. Analysis of PFOA at 1 to 25 ng/mL
 - (a) HPLC and the Mass-Spectrometer
 - (b) Calibration curve for PFOA analysis
 - (c) SPE methods for PFOA samples from impinger solutions and XAD resin trap (*see Appendix*).
 - (d) SPE methods for PFOA samples from Accelerated Solvent Extraction experiments (*see Appendix*)
4. Results and Discussion – pg. 7-10

Details of the numerous experiments that were run to gain knowledge and understanding of the interconnected issues are placed in the appendix.
5. Conclusions – pg. 10-11
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INTRODUCTION:

The goal of this project is to determine if perfluorooctanoic acid (PFOA) is generated as a degradation byproduct from polytetrafluoroethylene (PTFE) when heated to just below the onset of its melting point.

A joint working group composed of Environmental Protection Agency (EPA) members and fluoropolymer industry representatives developed a guidance document proposing a mass balance approach to this project. This mass balance approach consists of a quantitative analysis of PFOA content of the PTFE material prior to and post-heating. During the heating cycle, any PFOA present in the PTFE material or generated as a degradation byproduct is expected to be transferred from the heating chamber into impinger-type traps.

The difference in PTFE levels found between (a) the pre-heating and (b) the post-heating periods (including that in the traps and in the post heated sample) would, then, reflect the PFOA generated as a degradation product during the heating of PTFE.

Essentially, the mass-balance approach involves the analysis of the following samples:

- (A) PFOA in the original (pre-heated) sample, following the Accelerated Solvent Extraction or ASE (described later).
- (B) PFOA in the collecting traps (impinger solutions and XAD resin traps) transferred from the sample during the heating process (described later).
- (C) PFOA (retained or un-transferred from the heated sample), following the Accelerated Solvent Extraction.

Based on the above results, one could draw conclusions as to whether any PFOA is generated during the heating of PTFE under specified conditions.

If (B) + (C) remain the same as (A) or be less than (A), no PFOA is generated under the experimental conditions.

If (B) + (C) exceeds (A), PFOA is generated under the experimental conditions.

We were asked to develop a rugged reproducible method based on the suggestions in the guidance document.

ACCOMPLISHMENTS SO FAR AND PROBLEMS OVERCOME:

(A) Accelerated solvent extraction (ASE) method for determining residual PFOA in a PTFE samples was developed earlier by (Larsen, Kaiser, Botelho, Wooler, and Buxton, *Analyst*, **130**, 59-63, 2005; Larsen, Kaiser, Botelho, Bachmura, and Buxton, *Analyst*, **131**, 1105-1108, 2006). The ASE equipment was purchased and the ASE technique was successfully employed in the analysis of PFOA in several PTFE samples. (Details are provided later).

(B) A method for quantitative analysis of PFOA at 1 ng/mL. The primary requirement for evaluating any transfer of PFOA from the heated chamber into the trap is a method for accurately determining the PFOA in the impinger-trap solutions, as well as what was left un-transferred in the sample chamber. An excellent LC-MS method for quantitative analysis of 1 to 25 ng PFOA one mL of water was successfully developed. (Details are provided later. See Appendix)

(C) Evaluation of Efficiency of Transfer of PFOA from the sample heating chamber into the impinger-trap water. As recommended in the guidance document, the instrument set-up for the heating cycle required controlled heating, measured airflows and constant relative humidity (%RH). The temperatures at which PFOA generation was to be studied were determined by differential scanning calorimetry (DSC) and ranged from 280-315°C.

Most of our efforts at 3M, therefore, were directed toward adopting the equipment design suggested in the guidance document and modifying it as needed for quantitative transfer of 100 ng of PFOA from the sample heating chamber into the impinger-traps. Accomplishing quantitative transfer of PFOA at such low levels is vital and absolutely necessary for any correct interpretation of results. This point is well demonstrated by the results that we had obtained in course of this study. We encountered situations in which the PFOA at the low levels we were working with, was either (a) *destroyed* at higher temperatures or (b) *adsorbed* on the glass surfaces and would *not* be amenable to transfer to the trapping solution. Eventually after a long series of experiments in order to understand all the complexities, very recently we were able to accomplish quantitative transfer of 100 ng quantities of PFOA from the heating chamber into the trapping fluid. This quantitative transfer was achieved by using SigmacoteTM to passivate all glass surfaces coming in contact with PFOA.

All these necessary experiments, which were many, had taken a long time to complete because of the 24 hour duration of the heating cycle in some experiments. Details are provided later in the appendix.

EXPERIMENTAL

A. Accelerated Solvent Extraction

During ASE extractions of PFOA (Larsen *et al.*, *loc. cit.*) the PTFE material is heated to 150°C for 24 hours prior to the initial methanol extraction. PTFE is then extracted using methanol (MeOH) and the Dionex ASE system. The system moves the PTFE, which is located within a stainless steel cell sandwiched between special filter material with purified sand (Ottawa sand), into an oven where the temperature is raised to 150°C. MeOH is then introduced into the cell and the cell pressure is raised to 1500 psi. MeOH is forced through the PTFE sample bed and collected in 40 mL glass reservoirs. The guidance document requires multiple extractions to the point where less than 5% of the initial recovered value remains. In our experience, this has required four complete cycles of preheating and extracting. One run, then, by this complete method **needs** 8-10 days for a single analytical determination.

B. Equipment for PFOA Generation Testing. & Transfer/Collection of generated PFOA.

The equipment is designed to heat the PTFE material to predetermined temperatures and specified humidity and air-flow conditions and to quantitatively sweep the PFOA (background and heat-generated PFOA) into a trapping solution and then determine the PFOA so collected.

Apparatus that was assembled involved the use of “zero air” at 100 mL/min flow from a regulated air supply through two Aalborg airflow controllers. From the Aalborg flow controllers, the air moved through a humidification chamber and then passed through a heated transfer line into a GC oven prior to being introduced to the reaction vessel. A LabView software feedback loop was established with the oven temperature, which fed back temperature control to the heated transfer line, thus holding the heated transfer line to within 1°C of the actual oven temperature. The transfer line in the oven was connected to the reaction vessel of choice, which is where all tested PFOA or PTFE material was initially introduced. A Hewlett-Packard Gas Chromatography (GC) oven was modified to hold the reaction vessels, provided with connections for introduction of air, and an outlet (held at constant temperature) leading into an impinger train (1 to 3 impingers). See Figure 1 in Appendix for the assembly of the equipment.

The PTFE materials varied in PFOA concentration, but were generally targeted at 100 ng/mL within the reaction vessel.

Each impinger contained 20 mL of ultra pure (PFOA-free) water, where the transported PFOA was to be collected.

De-ionized water was further purified by pumping it through a C-18 HPLC column to remove residual PFOA. This water will be referred to as ultra pure water or C-18 water. The impingers were placed in an ice bath and kept at constant temperature near 0°C. To verify if any PFOA was being transported beyond the impinger train, an XAD resin column was placed on the very end of the last impinger, which then exhausted to atmosphere. All data parameters generated by the system (air flow, %RH, oven temperature, mixing chamber temperature, ice bath temperature, reaction vessel temperature) were compiled and retained within LabView software.

C. Analysis of PFOA at 1 to 25 ng/mL.

(a) HPLC and Mass Spectrometer specifications.

The specifications for running both the instrumentations were as follows.

HPLC:

Finnegan Spectra System LC

Column: ACE C-18, 5 micron, base-deactivated column

Flow Rate: 250 uL/min

Buffer: 49% 2mm Ammonium Acetate

Organic: 51% Acetonitrile

Injection Volume: 12 uL

Mass Spectrometer:

Finnegan Triple Stage Quad (TSQ)

Ions Monitored: PFOA (413 amu)

¹³C PFOA IS (415 amu)

Tuning & optimization per manufacturer's recommendations

After all samples have been run through SPE, they were analyzed by High Pressure Liquid Chromatography-Mass Spectrometry (LC-MS).

(b) Calibration curve for PFOA

A typical calibration curve is provided in Figure 2 in the Appendix.

(c) Standards and sample preparation

Standards and sample preparation and SPE methods used for extraction of PFOA prior to injection into HPLC and Mass-spectral analysis are provided in the Appendix.

DISCUSSION:

I. Determination of PFOA at ng/mL levels.

PFOA at the above levels can be confidently determined as demonstrated in Figure 2 (Appendix).

II Accelerated Solvent Extraction

Previously published extraction work on residual PFOA in PTFE had been successfully carried out using a Dionex Accelerated Solvent Extractor (ASE), so this technique was used. Concerns over potential contamination of the Extractor in the 3M Central Research Analytical Lab led to the acquisition of a new Dionex ASE. Exhaustive extractions were carried out by heat aging of the polymer at 150°C for 24 hours, then subjecting the sample to a pressurized methanol extraction cycle at 150°C. Following the initial extraction, subsequent ASE extractions were to be completed until less than 5% of the amount of initially extracted PFOA remained. In our experience with the PTFE materials tested, this required four complete ASE extraction cycles. PFOA recovery was enhanced by preheating for 24 hours at 150°C between extraction cycles. Therefore, to complete a full extraction cycle using the required preheating, ASE extractions and LC-MS analysis required a full 8-10 work days.

III. PFOA Generation and Testing

(a) The set-up of the equipment for testing the generation of PFOA from PTFE

The joint working group proposal specified that we should put together for this study a device assembled from components already commercially available. A commercially available thermal desorber unit was provided to us to allow all PTFE test samples to be held at specific temperatures for specific periods of time. The thermal desorber unit temperatures were not stable, and the unit was replaced by a Gas Chromatograph (GC) oven where tighter temperature control was achieved. Clean, moisturized air was introduced into the PTFE containing chamber through a heated transfer line under controlled flow conditions using two Aalborg mass flow control units. The desired percent relative humidity (%RH) was achieved through balancing the airflow using the two mass flow controllers and a humidification chamber. The outlet air stream was directed to a series of impingers to collect PFOA released from the test substance. The equipment is described in Figure 1 (Appendix).

LabView software was successfully programmed to accept feedback from multiple thermocouples (heated zones) as well as other data input devices to record % relative humidity and airflow. LabView software was used in a continuous feedback circuit from the GC oven temperatures to regulate the heated transfer line. This successfully raised the air temperature of the heated transfer line airflow being introduced

into the reaction vessel, thus maintaining the same air temperature as the oven temperature.

(b) Keeping the baseline level of PFOA as low as possible

The working group draft proposal specified that the baseline level of residual PFOA be determined in the test system and that the baseline PFOA be determined following standard cleaning protocol.

Baseline PFOA needed to be reduced to levels less than the minimum detectable limit. This required additional purification steps, such as

- (a) Deionized water was further purified by passing it through a C-18 HPLC column to remove any background PFOA. Un-purified de-ionized water was found to contain ~1.3-2.1 ppb of PFOA as shown in the appendix. Following the above purification step, PFOA was undetectable.
- (b) Air was passed through activated charcoal filtration.
- (c) Typically, threaded joints in this type of equipment are assembled using PTFE tape. Due to concern about background PFOA, the fittings were disassembled, cleaned with methanol (MeOH), and reassembled using epoxy resin to achieve airtight seals.

The overall PFOA background level was indeed undetectable.

(c) Transport Efficiency

Temperature and other co-factors:

Transport efficiency of PFOA material was to be evaluated at various temperatures and flow conditions on the basis of % recovery of PFOA in the impinger solutions.

Low recovery of the PFOA *per se* (added to the heating chamber) during transport testing indicated problems with the transport efficiency of the PFOA in our system as designed. This required us to explore various possible influencing factors such as air-flow rates, rate of introducing (generating) PFOA into the heating chamber, different temperatures, etc. as described in the experiments (shown in the appendix).

Direct slowly progressing injection of PFOA using fused silica lines with a syringe pump into the reaction vessel at elevated temperatures provided no greater recovery of PFOA when compared to direct addition of PFOA to the flasks at initial temperatures. Evaluation of slow versus rapid infusion of PFOA into the reaction vessel showed no significant differences.

Elevation of temperatures appeared to accelerate the decomposition of PFOA when in contact with glass surfaces.

The impinger outlets were fitted with glass frits to decrease the bubble size emerging from the impinger tips. However, low recovery of PFOA in the impinger train was experienced, raising questions about the trapping efficiency from the airflow.

To improve the efficiency of trapping PFOA, we fitted the impinger inlets with glass frits to decrease the size of the emerging bubbles. However, low recovery of PFOA in the impinger train was experienced, raising questions about the trapping efficiency from the airflow.

To test whether PFOA was moving through the impinger water without being successfully trapped, we added a Supelco XAD resin particle trap to the end of the impinger train. The PFOA was not being trapped in the impingers or on the XAD resin. Therefore, we suspected the PFOA was not reaching the impingers. Either the PFOA was being decomposed or it was binding to the glass surfaces of the reaction vessels or the glass connections beyond the reaction vessel.

Temperature studies were conducted at 50°C, 100°C, 150°C, 200°C and 300°C. PFOA was determined in the impinger solutions (transported PFOA), as well as what was retained in the heating chamber. We came to two conclusions, that at high temperatures (< 200°-300°C), PFOA is being destroyed and at lower temperatures, it is being adsorbed on to glass surfaces (walls of the chamber) and not readily available for efficient transport.

Overcoming adsorption of PFOA on glass surfaces

(a) Exploring replacing glass with quartz

In an attempt to avoid or reduce the number of active sites encountered on glassware, the suggestion was made that we evaluate the use of quartz glass. The 3M glass shop built several quartz reaction vessels and quartz connections. The use of quartz glassware by itself did not significantly improve recoveries.

(b) Surface treatment of glass with strong acids

On the premise that the adsorption of PFOA on glass surfaces may be based on its high acidity, prior passivating the glass surface with another strong acid was explored. Deactivation with dilute acid (1 N HCl) did not show improved recovery of the PFOA under various experimental conditions. Deactivation of active sites on the glassware with strong acid (50% sulfuric acid) improved recoveries (>90%) of PFOA when tested with 100 ng PFOA under vacuum using a cold finger apparatus with no airflow. This suggested the importance of surface treatment to prevent adsorption of PFOA on untreated glass surfaces. This led us to the next silanization step.

(c) Silanization of glass

To maintain adequate temperature control, stable airflows, and the required conditions of relative humidity, we returned to our original equipment design using the GC oven and quartz reaction vessels. To deactivate the glassware and avoid the use of highly concentrated acids, we resorted to using chlorinated organopolysiloxane solution in heptane to passivate the glass surfaces.. This treatment enhanced recovery of PFOA. We have been recovering greater than 90% of PFOA test material using silanized quartz glassware, in our original oven and at original airflow configuration during multiple runs of PFOA at 150°C and using 100 ng PFOA. Careful use of the silanizing agent followed by heating the glassware at 100°C has improved our ability to meet the desired sensitivity limits suggested in the protocol.

CONCLUSION:

We have found that at ng/mL levels, PFOA is not readily amenable to transfer in glass vessels. PFOA appears to react with and adsorb onto active sites on clean glassware. PFOA appears to react with active sites on quartz glassware as well. The form of salt used (Ammonium salt vs. Potassium salt) of PFOA does not appear to change this reactivity, nor does the use of the free acid form of PFOA.

PFOA standards prepared in methanol vs. standards prepared in water show no significant differences relative to recovery after heating under the conditions established for temperature and airflow. Standards prepared and stored in polypropylene showed no greater recovery than methanol standards prepared and stored in glass.

Extensive efforts and research into methods to recover PFOA under the conditions suggested by the guidance document of controlled temperature, constant airflow and constant humidity have been mostly investigated. Many obstacles have presented themselves along the way and we have had to change our methods to overcome low recoveries experienced early on in our investigations. The difficulty of meeting the desired sensitivity of 1 ng/mL has proven most challenging, forcing us to design and redesign our equipment. The stability of PFOA at the elevated temperatures assumed in the guidance document may be in question. It now appears that PFOA may be degrading below the temperatures called for in the experiments designed in the guidance document. However, further research and additional testing using passivated glassware is required. Conditions of elevated temperatures and controlled conditions of humidity will be fully investigated now that acceptable recoveries of PFOA have been achieved using known standards of PFOA and silanized glassware. The successful silanization of the active sites found in clean glassware may be the key needed to conclude the initial phase of this project.

In the light of the above mentioned fortuitous observation that PFOA is destroyed at higher temperatures (above 200-300°C) and since the temperature of incineration of PTFE materials is about 300°C, is it possible that even if any PFOA

is generated during the incineration phase, it is all perhaps quickly destroyed and poses less environmental concerns? However, we are aware that our observations are related to trace levels of PFOA and not to high levels of PFOA. This may require further investigation.

Appendix

Figure 1. – pg. 12-19

Figure 2. – pg. 20-21

Table I. – pg. 22

Table II. – pg. 23

Standard and Sample Preparations – pg. 24-26

Details of Experiments, Data & Results – pg. 27-55

Standards & Sample Preparation

Standards

Calibration Curve: 1 ng/mL to 25 ng/mL PFOA
IS: 10 uL of 1.0 ng/uL ¹³C PFOA (Haskel #25617)

Sample Prep

- Step 1** **add 20 mL of C-18 H₂O**
- Step 2** **add 1mL 1.0 N Formic Acid**
 -Vortex vials
- Step 3** **add 500 uL Saturated Ammonium Sulfate**
- Step 4** **add 2 mL of 50% Acetonitrile / 50% C-18 H₂O solution to standards**
 and blanks (to compensate for 2 mL solution used to rinse impingers)
 -Vortex vials

Note: For the actual sample preps the 2mL of Acetonitrile solution will be the rinse from the impingers & glassware

SPE

- Step 1** **Condition SPE**
- 1 mL Methanol (MeOH)**
 1 mL Acetonitrile (ACN)
 1 mL C-18 H₂O
- Step 2** **Load Sample**
 Rinse vials with 5 mL of 15% Acetonitrile
 -vortex 20 mL vials
- Step 3** **Wash SPE**
- 2x rinse SPE with 2 mL of C-18 H₂O**
 Rinse SPE with 2 mL of 15% Acetonitrile
 Centrifuge SPE cartridges
- Step 4** **Elute SPE**
- 0.3 mL 0.1 M Ammonium Acetate**
 0.3 mL Acetonitrile
 0.3 mL Acetonitrile
 0.3 mL C-18 H₂O

Sample preparation and SPE methods used for mass balance testing of PFOA from ASE extractions were as follows:

SPE Method for ASE Extraction for Thermal Degradation of PFOA

Calibration Curve: 5 ng/mL to 100 ng/mL PFOA
IS: 8 uL of 5.0 ng/uL ¹³C PFOA (Haskel #25617)

Standard & Sample Prep

- Step 1** **Add 2 filters to bottom of each cell, add sand, add filter to top, tighten**
Condition cells w/ *ASE Method 1 – flush w/ 100% MeOH
- Step 2** **Mix 500 uL of C-18 H₂O w/ IS & stds: add to middle of sand**
Add 8 uL IS directly to sand w/ solid samples
Run *ASE Method 2
- Step 3** **Remove solutions run through ASE and to each:**
Add 1 mL 0.5% 1.0 N KOH in C-18 H₂O (Dyneon H₂O)
Dry down samples & stds w/ LabConco RapidVap to remove MeOH
- Step 4** **To residual aqueous remaining from dry down step:**
Add 1 mL of 1.0 N Formic Acid
Add 100 uL Saturated Ammonium Sulfate
-vortex & run through SPE

SPE

- Step 1** **Condition SPE**
- 1 mL MeOH**
 1 mL Acetonitrile
 1 mL C-18 H₂O
- Step 2** **Load Sample**
Rinse vials with 2 mL of 15% Acetonitrile
-vortex
- Step 3** **Wash SPE**
- 2x rinse SPE with 2 mL of C-18 H₂O**
 Rinse SPE with 2 mL of 15% Acetonitrile
 Centrifuge SPE cartridges

Step 4 Elute SPE**0.3 mL 0.1 M Ammonium Acetate****0.3 mL Acetonitrile****0.3 mL Acetonitrile****0.3 mL C-18 H₂O****Standard ASE instrument parameters used during extractions:*****ASE Method 1****(To precondition cells)**

Preheat: 0 min
Static valve closed
Heat: 7 min
Static: 5 min
Temp: 150°C
Flush: 100% volume
Pressure: 1500 psi
Purge: 240 sec
Cycles: 1
Solvent A: 100% Methanol

***ASE Method 2**

Preheat: 0 min
Static valve closed
Heat: 7 min
Static: 5 min
Temp: 150°C
Flush: 50% volume
Pressure: 1600 psi
Purge: 240 sec
Cycles: 4
Solvent A: 100% Methanol

Data and Results

November 2005

Run #1:

11/17/05

The initial apparatus was in the process of being assembled. This run was used to check to see if the LabView software correlated with the actual read temperatures in: the mixing chamber, the transfer line, the reaction vessel, and the GC oven. A reaction vessel thermocouple was inserted into the reaction vessel to see if the temp of the reaction vessel was the same as the oven. Also, the % relative humidity was checked in the mixing chamber as well. Each of the three impingers was filled with 20 mL of bottled H₂O, and the flow rate was 200 mL/min (for Runs 1-7). The oven's initial temp was 50°C, and then it was ramped up to 150°C for 2 hrs. Then the oven was ramped up to 295°C for 8 hrs. It was intended to be held for 24 hrs, but the program failed on the GC oven. We needed to fix the program.

Run #2:

11/18/05

We reran the apparatus as in Run #1. The oven's initial temp was 50°C, ramped up to 150°C for 2 hrs, and ramped up to 300°C for 3.5 hrs. We checked to see if the offset on the oven temp could produce exactly 300°C. We found the offset to be 5°C. (Oven temp reading = 305°C; LabView actual reading = 300°C.) This offset was to be noted in all future experiments.

Run #3:

11/21/05

We wanted to see if the program could hold at a certain temperature for an indefinite period of time. There were errors throughout this run. The oven failed to hold at 300°C for more than 8 hrs (600 min). This was due to program limitations that we were able to overcome by changing our programming steps.

Run #4:

11/22/05

To check for more experimental offsets, and verify if the temperature inside the reaction vessel was the same as inside the oven, the oven was ramped up to 150°C from 50°C and was held at 150°C for 2 hrs. Then it was ramped up to 300°C and held

successfully there for 24.5 hrs. Then it was cooled back to 50°C. This run verified the temp inside the reaction vessel was the same as the temp inside the GC oven.

Run #5:

11/28/05

The reaction vessel thermocouple was now removed from the reaction flask, since Run #4 verified the temp in the reaction flask was the same as in the oven. This thermocouple was placed into an ice bath and from now on will be used to check the temperature of the impinger ice bath. Now it will be referred to as the "Ice Bath Thermocouple". Fused silica was fed down from a syringe inlet into the reaction flask. MeOH was added throughout the run through the fused silica. This was a dry run. The oven was ramped up to 150°C from 50°C and held for 2 hrs. Then it was ramped up to 300°C for 21 hrs and cooled back to 50°C at the end. This procedure for temp ramping was to be followed until further notice. Each impinger was filled with 20 mL of bottled water. The results showed PFOA contamination in all 3 impinger extracts. Glassware was thoroughly rinsed prior to the next extractions, as this could have been an issue.

Run #6:

11/30/05

To test for PFOA contamination in our system, each impinger was filled with 20 mL of bottled water and 100 uL of 1 N KOH. The airflow controllers were set to 106 mL/min (100% RH) and 94 mL/min (0% RH), for airflow of 200 mL/min. Before SPE, the KOH in these impinger extracts were neutralized with 110 uL of 1.0 N Formic Acid. MeOH was run through the syringe during the 150°C hold. Results showed <1 ng/mL PFOA contamination in all 3 impingers. It is possible we will be unable reduce PFOA contamination below 1 ng/mL, as the air in the room itself may be contaminated.

December 2005**Run #7:**

12/5/05

To further test for PFOA contamination in our system, 20 mL of bottled H₂O and 100 uL KOH were put into each impinger. 300 uL of MeOH w/ 10 ng/mL PFOA (Amm. Salt) was injected through a syringe pump during a 150°C hold, then 300 uL of MeOH was used as a rinse through the fused silica line as well. The flow rate was 200 mL/min. 1 mL of the 50% ACN was used to rinse the 1st impinger. 2 mL of the 50% ACN was used to rinse the 2nd and 3rd impingers. The transfer line leading out of the oven into the first impinger was rinsed w/ 1 mL of 50% ACN and added to the 1st impinger extract. The results showed that the blanks (Internal Std only, and double blank) of just the bottled water had ~100,000 area counts, which was unusual. 12.15 ng/mL PFOA total came out of the system through the impingers. About 1.3 ng/mL is background, while about 0.8 ng/mL is an unknown contaminant. We shouldn't have had more than 100% recovery, but we did.

ASE Run #1:

12/12/05

This was a test run to see if we could get the ASE to function. PTFE o-rings were replaced with fluoroelastomer o-rings in all of the rinse vials. 2 filters were placed on the bottom of the 11mm cells. Ottawa sand was added to ~3mm from the top of each cell, and another filter was placed on top. (Note: K letter is always on top when running these cells through the ASE.) The cells were preconditioned using "ASE Method 1". The ASE failed – we received varying levels of solvent in each resultant vial at the end of the run.

LabConco Rapid Vap Test:

12/9/05

To test our Rapid Vap instrument, 5 mL of MeOH was added to 0.5 mL of H₂O. The MeOH was evaporated off using the Rapid Vap, and a standard curve was extracted using SPE. 8 uL of 5 ng/mL PFOA IS was used, and the curve was run from 5-100 ng/mL. We wanted to see if we could evaporate off the MeOH and still successfully extract the PFOA through SPE. The resulting standard curve had an R=1.0000. The Rapid Vap will be used for drying down MeOH in the future.

Run #8:

12/14/05

20 mL bottled H₂O and 100 uL KOH were added to each impinger. This was a dry run. Glassware was rinsed as before and will continue to be rinsed the same way as Run #7 in all future experiments until further notice. The flow rate used was 50 mL/min, and didn't change until further notice in future experiments. The results showed the Int. Standard Only and double blanks had ~200,000 counts in each impinger, which was higher than anticipated. ~500,000 counts were found in each impinger. ~6 ng/mL was found total (~2 ng/mL in each impinger). We needed to change the water we were using – we received too high background counts. From then on, we used the Finnigan LC-MS to filter the bottled water to add to all reagents used in future experiments and the system to reduce background counts. Further investigation indicated the purchased bottled water was the source of the background PFOA counts. The bottles come sealed with a PTFE-lined cap. To eliminate the background PFOA levels, we used a C-18 HPLC column and pump to remove the PFOA. All water for reagents and impingers now is routinely pumped through the C-18 HPLC column prior to use. After 4 L of bottled water and/or Milli-Q water has been pumped through the C-18 HPLC column, the column is rinsed with 20 mL of methanol and rinsed with C-18 pumped water prior to being used to remove PFOA from the next 4 L of water. This purified bottled water / Milli-Q water will be referred to as C-18 purified water (C-18 water) from here on in this summary report.

Run #9:

12/19/05

20 mL of bottled filtered H₂O from the LC-MS was added to each impinger w/ no base added. This was a dry run. Results showed ~2.3 ng/mL PFOA present in each impinger (area counts = 227,000-400,000). The run was accidentally ramped down to

50°C after 6 hr at 300°C (not set properly). The ice bath thermocouple was taken out of the ice bath water by accident overnight. Results showed w/ the C-18 H₂O there was still between 1.74 and 2.85 ng/mL of PFOA in each impinger. PFOA contamination was apparent.

ASE Run #2:

12/27/05

We wanted to see if the ASE would function again. Cells were preconditioned w/ Method 1. Then, "ASE Method 2" was used to run the samples. To the standards and blanks, 8 uL of 5 ng/uL PFOA IS was added and a standard curve from 5 to 100 ng/mL was created. 500 uL of C-18 H₂O and 100 uL of saturated ammonium sulfate were also added to each standard and blank and were then vortexed. Addition of saturated ammonium sulfate (SAS) decreases the aqueous solubility of PFOA. We tried using SAS in this run to see if we could obtain good recoveries. The run worked successfully. However, the SAS was insoluble in the methanol and formed salt crystals in the collection vials. The decision was made to stop adding SAS to the ASE samples as a result of the SAS crystal formation. Samples were introduced dry to the sand. Both samples and standards were added in the middle of the sand (some sand was removed from the conditioning step, solution added, sand replaced on top). The run worked successfully, but, as noted, salt was produced in the collection vials due to the 100 uL SAS reacting with the insoluble MeOH.

ASE Run #3:

12/28/05

This was a rerun of "ASE Run #2", except no SAS was used. Cells were preconditioned w/ Method 1 and Method 2 was used as the run parameters. 5 mL cells were used this time, and in Method 2, the "Flush" parameter was changed to 50% volume due to the ASE's inability to differentiate between a 5 mL cell and an 11 mL cell. Samples added had approx. 50 mg PTFE in each. Standards and blanks were run as in ASE Run #2. The run time was approximately 34 min/sample cell (total time = 6.8 hrs for 12 samples). Approximately 18 mL of sample was found in each collection vial at the end of the run. The solvent used was 100% MeOH. The samples were added to their respective cells by removing ½ of the conditioned sand, placing in the samples, and then adding ½ the sand back on top.

After the samples were run through the ASE, the MeOH was evaporated off and the samples were dried down using the LabConco RapidVap w/ a vacuum pump. Before the dry down step, 500 uL of 1 N KOH in 100 mL H₂O (Dyneon H₂O) was added to every tube to concentrate the standards and samples. All of the samples were "bumped" at some time in the RapidVap – it's unknown exactly how much was lost. After the dry down step, 500 uL of C-18 H₂O, 1 mL of C-18 1.0N Formic Acid and 100 uL of SAS were added to each remaining sample. The samples were then run through SPE as before. Results showed a good curve for the standards. However, the PFOA Dyneon samples showed very little presence of PFOA (<0 ng/mL). Sample 1 showed 0.105 ng/mL, but that is questionable due to bumping and loss of most of the sample in the dry down step.

January 2006

ASE Run #4:

1/4/06

This was a repeat of ASE Run #3 exactly. 100 uL SAS was added and again remained in the vials. To compensate, 1 mL of Dyneon H₂O was added to every tube along with 1 mL of C-18 H₂O. This successfully dissolved the salt precipitate. The RapidVap step produced no serious "bumping" this time due to not adding more than 7 mL solution to each tube at a time. (Note: ~20 mL solution results from the ASE run.) After the dry down step, 1 mL of C-18 1.0 N Formic Acid was added to each tube (pH=2.40). The final results showed <0.269 ng/mL PFOA in all three sample runs (<0 ng/mL in samples 1 & 3.)

Run #10:

1/4/06

20 mL C-18 H₂O was added to each impinger. This was a control run (no PFOA added). Results showed impingers 1 & 2 had ~3.5 ng/mL PFOA present and impinger #3 had ~1 ng/mL present (area counts: 83,000-291,000). The ice bath thermocouple moved out of the bath again overnight. Much care will be taken in the future to keep the thermocouple in the ice bath for the entire 24 hrs.

Run #10b:

1/5/06

20 mL C-18 H₂O was added to each impinger. This was another control run, but the only airflow was through both humidifying chambers directly into the impingers. The transfer line and oven were not included in this run. It was temperature independent and kept at room temp constantly. The humidity fluctuated throughout the 24 hr period due to inconsistent airflow. The results showed ~3.5 ng/mL total in all 3 impingers combined: which means contamination was present in this portion of the system, along with the oven and transfer line portion as well.

Run #11:

1/10/06

20 mL of C-18 H₂O was added to each impinger. It was another control run as in Run #10. Results showed <1 ng/mL PFOA in all 3 impingers. The system has been cleaned well to reduce background.

Run #12:

1/11/06

We now were ready to try to move a PFOA standard with a higher concentration. 20 mL of C-18 H₂O was added to each impinger. 100 uL of 0.5 ng/uL PFOA Ammonium Salt standard @ 10uL/min was moved through the syringe inlet @ 150°C. The fused silica line was cleaned with 100 uL of MeOH @ 10 uL/min immediately following. The flow rate was 50 mL/min. The results showed 10.89 ng/mL PFOA was recovered in the 3 impingers (21.78% recovery). 50 ng/mL was what should have been

seen. PFOA was lost somewhere – either it passed through the impingers or it did not reach the impingers.

ASE Run #5:

1/13/06

This run we wanted to add PTFE material to the cells to see what concentration of PFOA was in them. Methods 1 and 2 were used as before. This time, 2 samples of ~50 mg PTFE and 2 samples of ~100 mg PTFE were added. 1 mL of 1 N KOH was added before the dry down step. 1 mL of C-18 1 N Formic Acid and 100 uL SAS were added to each tube after the dry down step. Results showed ~150 ng/mL in 3 of the 4 samples. 1 sample was bumped during dry down – most of the IS was lost. We would expect ~100-200 ng/mL in all samples, so this run was informative.

Run #13:

1/16/06

We tried to move a higher concentration of PFOA standard again. 50 ng/mL at 100 mL/min flow rate was injected through the fused silica line. The line was rinsed w/ 100 mL MeOH. We checked all the fittings in the system prior to the run and found the actual flow rate going through the impingers was 97 mL/min, whereas the read flow rate was 100 mL/min (97% accuracy). Results showed 15.38% total recovery in the impingers. Looking at the data, it appears that the PFOA is possibly being blown either entirely out of the system through the impinger train, it doesn't even make it out of the reaction flask, or it is decomposing in the reaction flask.

ASE Run #6:

1/17/06

To elaborate on the results of "ASE Run #5", we used the same procedure as before, except the 10 uL of IS was added to 500 uL C-18 H₂O before adding it to the sample cells. 2 samples of ~12 mg (samples 3 & 4), 1 sample of ~25 mg (sample 2), and 1 sample of ~50 mg (sample 1) were added. This time, 1 mL of 1 N KOH was added instead of 0.5% 1 N KOH before the dry down step accidentally. So, 3 mL of 1 N FA were added to compensate for basicity of mixture after dry down (pH = 3-3.5). 100 uL SAS was still added. Results showed 140 ng/mL in sample 1, 66.2 ng/mL in sample 2, and 35.9 and 34.2 ng/mL in samples 3 and 4. We expected this pattern to develop, so these were good results.

PFOA Room Temp Test:

1/17/06

We wanted to see how much PFOA contamination was in the air in the lab. We placed 20 mL of C-18 H₂O into impingers and hooked them together but left the rest of the system disconnected. We kept the system at room temp for 24 hrs and extracted through SPE as before. No airflow or heating was present. We found >6 ng/mL PFOA present in the impingers total. Was that caused by contamination of the glassware or by the air of the room itself?

Run #14:

1/19/06

We reduced the PFOA standard concentration used. 10 ng/mL PFOA was injected at 100 mL/min flow rate. Results showed 39.94% recovery in the impingers. There was much better recovery at 10 ng/mL than at 50 ng/mL at the same flow rate (100 mL/min).

Run #15:

1/20/06

Another test at higher PFOA concentration, 100 ng/mL PFOA was injected at 100 mL/min flow rate. Results showed 15.71% recovery only, but 13.7 ng/mL was in impinger #1. Recovery here was much worse than at 10 ng/mL, but similar to the values received at 50 ng/mL.

Run #16:

1/23/06

100 ng/mL PFOA was injected at 100 mL/min flow rate. This time, a Supelco filter plug (XAD resin) was placed at the end of the impinger train to see if any PFOA was being lost outside the system to the air and in what amount. The PFOA from the plug was extracted by rinsing it with 5 mL MeOH w/ a vacuum pump attached, and then added to a tube with 1 mL of Dyneon H₂O and IS. The MeOH was dried down using the RapidVap and 1 mL of Formic Acid (FA), and 100 uL of SAS were added to the extracts before being run through SPE. Results showed only 5.30% recovery in the 3 impingers, but 55.1% recovery in the XAD resin. The overall total recovery was 60.4%. This was very significant.

Supelco Filter Study (From Run #16):

1/31/06

We took the Supelco XAD resin from the end of the impinger train from Run #16 and added three 5 mL aliquots of MeOH through a filter, which was allowed to gravity drain into tube w/ 1 mL of 0.5% 1 N KOH and 50 ng/mL PFOA IS. The tubes were dried down by the RapidVap. 1 mL of 1 N FA and 100 uL SAS were added and the tubes were vortexed. Solutions were run through SPE with a standard curve from 5 to 100 ng/mL. Results showed 15.0 ng/mL, 12.6 ng/mL, and 12.6 ng/mL in each of the 3 aliquot extracts (Total = 40.2 ng/mL in Supelco XAD resin). 2 additional aliquots of MeOH had been previously evaluated at 10.1 ng/mL and 3.5 ng/mL PFOA. Overall, the total recovery of the extracted plug from Run #16 showed 55.1 ng/mL (or, 55.1% recovery). A blank Supelco XAD resin was also extracted using three 5 mL aliquots of MeOH. The total recovery of PFOA in the blank XAD was 2.0 ng/mL. Is this PFOA already present in the XAD resin, or is it just contamination?

ASE Run #7:

1/23/06

12 cells were conditioned with Method 1. Method 2 was used in a 5-cycle process where the cells were preheated for 24 hrs in another GC oven before each cycle

was run through Method 2. The goal was to see a definitive reduction in the amount of PFOA received in each collection vial after every cycle. 5.1 mg PTFE was added to sample 1, 12.6 mg was added to sample 2, 25.2 mg was added to sample 3, and 49.2 mg was added to sample 4. After Cycle 1, 27.9 ng/mL PFOA was found in sample 1, 68.0 ng/mL was found in sample 2, 129.3 ng/mL was found in sample 3, and 240.2 ng/mL was found in sample 4. Between each cycle run, the cells were placed into a GC oven for 24 hrs overnight at 150°C. After Cycle 2, 4.6 ng/mL PFOA was found in sample 1, 13.8 ng/mL in sample 2, 16.0 ng/mL in sample 3, and 38.0 ng/mL in sample 4. Or, looking at it quantitatively, sample 1 was 16.6% of what it was in cycle 1, sample 2 was 20.3%, sample 3 was 12.4%, and sample 4 was 15.8%. After Cycle 3, sample 1 was 0% PFOA of what it was in cycle 1, sample 2 was 0.7%, sample 3 was 3.6%, and sample 4 was 5.2%. Cycle 4 failed, as there was a pump failure, although it was seen that after approx. 4 cycles all samples should be reduced to <5% of what they were after the 1st cycle, a significant finding.

Run #17:

1/25/06

We wanted to change the airflow rates to see if that had any effect on the movement of PFOA. 10 ng/mL PFOA was injected at 50 mL/min airflow rate. Results showed 29.64% recovery in the 3 impingers. Lowering the rates of zero airflow did not increase recovery significantly; therefore, we decided to try increasing the airflow rate.

Run #18:

1/30/06

10 ng/mL PFOA was injected at 200 mL/min airflow rate. Results showed 48.32% recovery in the 3 impingers. In attempting to increase the airflow to 200 mL we experienced a significant increase in the loss of airflow through the system due to leaking of ground glass connections. A second consideration was the challenge concentrations of 10 ng/mL being too low of concentration. It was decided to use 100 ng/mL for future experiments due to possible losses to glassware surfaces.

February 2006**Run #19:**

2/2/06

This was a control run (no PFOA added) where Supelcarb HC Charcoal Filters were placed into the apparatus before the mixing chambers to hopefully clean out the PFOA leaching through the system from the compressed air tank. The total recovery after this cleansing run was only 1.526 ng/mL of background PFOA. The Charcoal Filters will remain in place for all future experiments.

ASE Run #8:

2/7/06

This run hoped to produce similar results to "ASE Run #7". Cells were conditioned with Method 1, and 4 cycles using Method 2 were run to look for a reduction in overall PFOA extracted in each subsequent cycle. TF2071 was the lot number for the PTFE samples tested. 11.9 mg PTFE was added to sample 1, 14.1 mg was added to sample 2, 24.3 mg was added to sample 3, and 25.6 mg PTFE was added to sample 4. After Cycle 1, 139.8 ng/mL PFOA was found in sample 1, 171.8 ng/mL was found in sample 2, 294.6 ng/mL was found in sample 3, and 298.0 ng/mL PFOA was found in sample 4. From this point on, only the 4 sample cells were preheated in the GC oven and run through subsequent cycles. After Cycle 2, 2.8% of sample 1 remained when compared to Cycle 1 results, 8.8% remained in sample 2, 9.8% remained in sample 3, and 10.5 % remained in sample 4. After Cycle 3, 0% (<0 ng/mL) remained in samples 1 and 2, 0.8% remained in sample 3, and 1.4% remained in sample 4. And after Cycle 4, <0 ng/mL remained in all of the samples. Apparently, 4 cycles of ASE with heating reduced the amount of PFOA present in the PTFE to less than the 5% value of the initial run. This meets the requirements of the proposed ECA protocol.

Affluent Flow Temp Study:

2/9/06

To check for the affluent flow temp at each impinger, the thermocouple was taken out of the ice bath and placed at the end of the impinger train and the temperatures were recorded as each impinger was removed one at a time. The temp in the oven was held at 300°C throughout the experiment. Results showed at the end of the 3 impinger train, the temp was 20-28°C; at the end of the 2 impinger train, the temp was 19-28°C; at the end of the 1 impinger train, the temp was 19-21°C, and at the end of the line out of the GC oven, the temp was 139-141°C. The data suggests there is no need for 3 impingers. We could possibly use only 1, as the temp is virtually the same at the end regardless if 1, 2 or 3 impingers are present.

Run #20:

2/14/06

100 ng/mL PFOA was injected at 100 mL/min flow rate. The impingers had frits added to the ends of them so the bubbles would be hopefully aspirated much smaller and would allow more contact with the water itself. The results showed 72.0 ng/mL in impinger #1 and 80.1% recovery overall. This is the best recovery we have seen yet by far, and we will use these frits from now on until further notice. However, caution was used by these results, as it is entirely possible that 1000 ng/mL PFOA was added by accident instead of 100 ng/mL. If this were the case, then ~10% recovery would be what was achieved. Further studies indicate strongly that this was the situation.

Run #21:

2/16/06

100 ng/mL PFOA was injected at 100 mL/min flow rate. The Supelco XAD resin was attached at the end of the 3rd impinger to hopefully collect more PFOA and improve recovery. The results showed only 8.64% recovery. There is a possibility that the recovery went down due to the syringe not being seated in the syringe inlet correctly.

Therefore, some of the PFOA standard was never pushed through the capillary into the oven.

Run #22:

2/20/06

This was a repeat of "Run #21". 100 ng/mL PFOA was injected at 100 mL/min flow rate. The Supelco XAD cartridge was also added and will be included in all future runs until further notice. Run #22 was a repeat of Run #21. The results showed only 4.81% recovery. The recovery possibly was low due to untightened fittings in the GC lines causing flow to leak out of the system, and the fact that the line coming out of the oven was not rinsed for PFOA. From now on, a Polypropylene adapter will be used when extracting the PFOA from the Supelco XAD resin because of its low blank background counts (10884.2 counts).

ASE Blank Sand Run:

2/20/06

To check to see if the Ottawa sand used for the ASE contributed any PFOA contamination to our results, 6 blank cells were conditioned through Method 1. They were then placed in the oven overnight for 24 hrs at 150°C. Then the cells were run through the ASE Method 2 and extracted through SPE. Results showed cells 1-5 had between 25412.9-69908.5 area counts (=0.32-0.89 ng/mL PFOA present). Cell 6 appeared to be contaminated. It appears that the Ottawa sand does not contain high enough background levels of PFOA to cause concern.

Run #23:

2/22/06

100ng/mL PFOA was injected at 100mL/min flow rate. This was a repeat of Run #22 to hopefully fix the GC line troubles. Results showed 7.61ng/mL in impinger #1, but only 8.24% recovery overall. PFOA is not being recovered from the apparatus.

Cold Trap V-1 Test:

2/23/06

We wanted to try a new approach to trapping the moved PFOA standard, so instead of using an impinger train in an ice bath ~0°C, a new cold trap apparatus with only 1 impinger was placed in a dry ice bath with isopropyl alcohol (~-80°C). The impinger train was replaced and we hooked up the end of this impinger with the line coming out of the oven. The same method was run as before, except that this new cold trap apparatus was used instead. 1.01 mL of H₂O was retained in the cold trap, which is what would be theoretically expected, proving that a dry ice bath may be used in place of an ice bath.

Run #24:

2/27/06

100 ng/mL PFOA was injected at 100 mL/min flow rate. This time the PFOA was introduced through the silica line at 100°C instead of at 150°C to see if this would cause better recovery. The entire GC oven program was ramped only to 100°C and then

was held at 300°C instead of being ramped to 150°C and then held at 300°C. Results still showed only 2.226% recovery.

Dry Ice Run #1:

2/28/06

The same apparatus that was assembled in the "Cold Trap V-1 Test" was rerun, except that in this case the 100 ng/mL PFOA @ 100 mL/min flow rate @ 100°C was injected and checked for recovery. The flask impinger was rinsed with 5 mL of 100% MeOH. The impinger showed only 2.57 ng/mL PFOA. Recovery is still a major issue that needs to be resolved.

March 2006**Dry Ice Run #2:**

3/1/06

We wanted to try a different type of PFOA standard to see if that made any difference on its movement. This was a repeat of "Dry Ice Run #1", except ¹³C PFOA linear free acid was used in place of the ammonium salt PFOA 3M standards that were used before. The impinger only showed only 1.18% recovery, so the free acid form did not improve recovery.

U-Tube Run #1:

3/2/06

A new type of cold trap was tested to try to improve recovery. A repeat of the "Dry Ice" runs, except a U-Tube held at -80°C was used as a collection means for PFOA in place of an impinger. The oven in this case was ramped up to 150°C and held for 1 hour after the injection of PFOA. The U-Tube showed 0.112 ng/mL PFOA, and the reaction flask & line out of oven showed 4.079 ng/mL. Total recovery was only 4.191%. The U-Tube did not improve recovery of PFOA.

Syringe Pump Recovery Test:

3/3/06

We wanted to check to see if the syringe pump was working properly and replaced the fused silica with a brand new one. We pumped the free acid PFOA in MeOH into a flask and 2 separate polypropylene tubes. The flask trial was capped for 2 hrs and held at room temp. All 3 trials were extracted with 5 mL of MeOH and were dried down by the RapidVap. After SPE extraction, the results showed ~100% recovery in all 3 trials. The syringe pump and fused silica were therefore eliminated as the cause of our poor recovery.

Run #25:

3/6/06

We wanted to see how much PFOA was remaining in the reaction vessel (oven flask) in the oven. 100 ng/mL PFOA free acid in MeOH was injected at 100 mL/min airflow, held for 2 hrs at 100°C and ramped up to 150°C for 22 hrs. Results showed 1.5% recovery in the impingers, 5.3% recovery in the XAD resin, and 87% recovery in the oven flask. Total recovery was 93.67 ng/mL PFOA. It still appeared that PFOA was not successfully migrating out of the oven to the impinger train. Total recovery vs. impinger recovery was unacceptably low, as most PFOA didn't migrate.

U-Tube Run #2:

3/7/06

A repeat of Run #25 exactly, except the U-Tube impinger replaced the impinger train and was kept chilled at -80°C in dry ice and IPA. Results showed only 1.95 ng/mL PFOA was collected in the U-Tube. It is probable the PFOA remained in the oven flask as Run #25 showed, but that was never checked. The U-Tube has not helped recovery of PFOA, so it will no longer be used.

PFOA Flask Heat Check:

3/9/06

We wanted to do a wide range of PFOA degradation tests with different standard types at different standard concentrations and temperatures inside sealed flasks in the oven with no airflow to see what effect each had on recovery.

Ten 125mL Erlenmeyer flasks were prepared as follows:

- 1) 100 ng/mL PFOA Free Acid in MeOH was injected into flask and held at room temp for 2 hrs.
- 2) 100 ng/mL PFOA Free Acid in H₂O was injected into flask and held at room temp for 2 hrs.
- 3) 100 ng/mL PFOA Free Acid in MeOH was injected into flask and held at 150°C for 2 hrs.
- 4) 100 ng/mL PFOA Free Acid in H₂O was injected into flask and held at 150°C for 2 hrs.
- 5) 500 ng/mL PFOA Free Acid in MeOH was injected into flask and held at 150°C for 2 hrs.
- 6) 500 ng/mL PFOA Free Acid in H₂O was injected into flask and held at 150°C for 2 hrs.
- 7) 100 ng/mL PFOA Free Acid in MeOH was injected into flask and held at 150°C for 2 hrs and then at 300°C for 2 hrs.
- 8) 100 ng/mL PFOA Free Acid in H₂O was injected into flask and held at 150°C for 2 hrs and then at 300°C for 2 hrs.
- 9) 500 ng/mL PFOA Free Acid in MeOH was injected into flask and held at 150°C for 2 hrs and then at 300°C for 2 hrs.
- 10) 500 ng/mL PFOA Free Acid in H₂O was injected into flask and held at 150°C for 2 hrs and then at 300°C for 2 hrs.

Results showed between 80-100% recovery for all samples 1-6 (those at held at room temp and at 150°C). It appears at room temp and 150°C the PFOA doesn't degrade readily. Results showed between 0-10% recovery for all samples 7-10 (those ramped up to 300°C). It appears the PFOA degrades and cannot be recovered at 300°C. We will need to test at what temp PFOA reaches its degrading point. All data is summarized in Table 1.

Run #26:

3/13/06

This run was similar to "Run #25". 100 ng/mL PFOA in MeOH was injected at 150 mL/min at 100°C for 2 hrs, and then was ramped up to 150°C for 22 hrs. Results showed 7.4% recovery in the impingers, 0.5% recovery in the XAD resin, and 57.3% recovery in the oven flask. Total recovery was 65.18 ng/mL. The PFOA is still not successfully migrating out of the oven to the impinger train. It should be noted that the back pressure caused by the frits on the ends of the impingers was very high, as only 127 mL/min was measured by a flow meter when the run began.

PFOA Flask Heat Check #2:

3/15/06

This was another group of PFOA degradation tests. Five 125 mL Erlenmeyer flasks were prepared. 100 ng/mL Free Acid PFOA in MeOH was injected into each flask, which were then capped and placed into the GC oven for 1 hr at 5 different temperatures: (175°C, 200°C, 225°C, 250°C, and 275°C). The results showed at 175°C, 81.0 ng/mL PFOA was recovered. At 200°C, 69.8 ng/mL was recovered. At 225°C, 60.1 ng/mL was recovered. At 250°C, 14.1 ng/mL was recovered. At 275°C, 12.2 ng/mL was recovered. It appears that between 225°C and 250°C, the PFOA degrades rapidly. All data is summarized in Table 1 and Figure 1.

Run #27:

3/16/06

We wanted to try adding PFOA directly into the oven flask again. 100 ng/mL PFOA in MeOH was added directly into the flask all at once at 100 mL/min (no syringe pump or fused silica was used). It was held at 150°C for 16 hrs. 4.5% recovery was found in the impingers. <0 ng/mL was found in the XAD resin, and 3.7% was recovered in the oven flask. Total recovery was 8.22 ng/mL. Since the PFOA was injected directly into the flask without the use of the fused silica, it's possible that the PFOA volatilized much faster than if it was injected over a 10 min span, even though the temp was kept at only 150°C.

PFOA Flask Heat Check #3:

3/20/06

This was an initial glassware acid treatment recovery study. Four 125 mL Erlenmeyer flasks were prepared. 100 ng/mL PFOA in H₂O was placed in two of the flasks, and 500 ng/mL was placed in the other two. The sides of 2 of the flasks (1 at 100 ng/mL and 1 at 500 ng/mL) were rinsed with 7 mL of 1 N HCl before they were heated. All flasks were capped and placed in the GC oven for 2 hrs at 225°C. The Bayer – Free Acid PFOA in H₂O was the PFOA type used. Results showed ~52% recovery in the 100 ng/mL flask w/ no HCl wash, ~100% recovery in the 100 ng/mL flask w/ HCl wash, and ~60% recovery in both of the 500 ng/mL flasks. It appears that the HCl wash does improve recoveries for the free acid in H₂O at 100 ng/mL, but there's a questionable advantage at 500 ng/mL. Results are shown in Table 1.

Vacuum Trap Test – V-1:

3/20/06

A vacuum trap apparatus was designed and built in the 3M glass shop to investigate the relative movement of PFOA. Two tubes of the same length were connected across a vacuum inlet tube (similar to the small letter “n”). This vacuum port was located in the center of the connecting cross tube. To one tube, 100 ng/mL PFOA was injected and frozen in a dry ice bath for 10 min at –80°C in IPA and dry ice. Then, vacuum was applied and all trapped air evacuated from the apparatus. The tube with PFOA was then placed in a thermal desorber and the temperature was ramped to 100°C for 16 hrs while the other tube was placed in a dry ice / IPA cold trap. The goal was to move the PFOA from one tube to the other, and see if the IPA migrated PFOA could be recovered. Results showed the cold trap only produced ~25% recovery in the recovery tube. However, the rest of the glassware when rinsed produced ~100% recovery. It appeared that the PFOA was not migrating.

Run #28:

3/22/06

This run was conducted to evaluate if PFOA standards kept in MeOH or in H₂O created better recoveries. 100 ng/mL Free Acid PFOA in H₂O was added directly into the GC oven flask at 100 mL/min flow rate and held at 150°C for 24 hrs (no syringe pump or fused silica was used). Two impingers were used. The one closest to the oven had a frit on the bottom, and the second one that led to the XAD resin did not have a frit. Results showed 5.8% recovery in the impingers, <0 ng/mL in the XAD resin, and 104 ng/mL in the oven flask. Total recovery was 109.8%. It appears the Free Acid in H₂O works better than the Free Acid in MeOH as it is suspected that the MeOH causes the PFOA to convert into a methyl ester (see Run #27). The Free Acid in H₂O will be the PFOA type used from now on until further notice due to findings from previous runs. Results are shown in Table 2.

Vacuum Trap Test – V-2:

3/27/06

A repeat of "Vacuum Trap Test – V-1" exactly, except that this time, the run lasted only 2 hrs. 100 ng/mL PFOA was introduced and the results showed 5.79 ng/mL in the recovery tube but 127 ng/mL still in the rest of the glassware (>100% recovery). So, it appears still the PFOA isn't migrating well using this apparatus.

Run #29:

3/28/06

To investigate if decomposition of PFOA was due to relative humidity in the zero air, 100 ng/mL PFOA was added directly into the oven flask as before in "Run #28". The flow rate was still 100 mL/min and it was held at 150°C for 24 hrs. However, in this run, the flow was dry air (<5% relative humidity). The results showed 4.7% recovery in the impingers, <0 ng/mL in the XAD resin, and 79.0 ng/mL in the oven flask. Total recovery was 83.73 ng/mL. The dry air didn't appear to help recovery in the impingers, but from now on the current 2-impinger method will be used.

Run #30:

3/29/06

A repeat of "Run #29" except this time the syringe pump and fused silica was used again to inject the 100 ng/mL PFOA at 100 mL/min dry air at 150°C for 24 hrs. The results showed 9.2% recovery in the impingers, 37.1% recovery in the XAD resin, and 5.5% recovery in the oven flask. Total recovery was 51.85%. This time better recovery was found, possibly due to the fused silica being used instead of direct addition of PFOA. However, we began to suspect PFOA degradation in the glass reaction vessels.

April 2006**Run #31:**

4/4/06

This was a repeat of "Run #30" exactly. 100 ng/mL PFOA at 100 mL/min dry airflow was injected at 150°C and held for 24 hrs. Results showed 41% recovery in the impingers this time, 3.41% recovery in the XAD resin, and 10.6% recovery in the oven flask. Total recovery was 54.74%. There was successful duplication of the previous run, though it is unclear why in this case most of the PFOA was recovered in impinger #1 (37.9 ng/mL), rather than in the XAD resin.

Run #32:

4/5/06

We wanted to see if we could deactivate active sites on the glassware and improve our PFOA migration by adding a concentrated acid to the oven flask prior to the run.

This run was a repeat of "Run 30" again except that before the run was started, the walls of the oven flask were rinsed with 5 mL of 1N HCl. The walls were left wet as the run began. 10 ng/mL PFOA was injected at 100 mL/min dry airflow at 150°C for 24 hrs. The results showed 5.4% recovery in the impingers, 2.2% recovery in the XAD resin, and 1.8% recovery in the oven flask. Total recovery was 9.48%. The HCl wash gave worse recovery. However, we believe there was experimental error in this run.

Run #33:

4/6/06

This was a duplicate rerun of "Run #32". Results showed 20.3 ng/mL PFOA in impinger #1, 0.6 ng/mL in impinger #2, 1.9 ng/mL in the XAD resin, and 46.2 ng/mL in the oven flask. Total recovery was 68.9 ng/mL. This time there was good overall recovery, but much of the PFOA was still remaining in the flask. The HCl was still not helping PFOA migration.

Run #34:

4/10/06

We started running a series of tests on how increasing the temperature in the GC oven helped or hindered PFOA migration and recovery. 100 ng/mL PFOA was injected at 100 mL/min dry airflow through fused silica. The run was held at 175°C for 24 hrs. There was no HCl wash of the flask. Results showed 12.6 ng/mL in impinger #1, 4.8 ng/mL in impinger 2, 11.4 ng/mL in the XAD resin, and 5.3 ng/mL in the oven flask. Total recovery was 34.11%. This was poor recovery, but the results were spread out more evenly.

Run #35:

4/12/06

100 ng/mL PFOA was injected at 100 mL/min dry airflow through fused silica. The run was held at 200°C for 24 hrs. There was no HCl wash of the flask. Results showed 6.48 ng/mL in impinger #1, 0.59 ng/mL in impinger #2, 1.87 ng/mL in the XAD resin, and 1.12 ng/mL in the oven flask. Total recovery was 10.06%. This was very poor recovery. Possibly the PFOA in H₂O degrades too much at 200°C.

Run #36:

4/13/06

Since increasing the temperature in the GC oven reduced our recovery of PFOA, we tried reducing the temperature lower than 150°C. 100 ng/mL PFOA was injected at 100 mL/min dry airflow through fused silica. The run was held at 100°C for 24 hrs. There was no HCl wash of the flask. Results showed 1.4% recovery in the impingers, 1.3% recovery in the XAD resin, and 97.6% recovery in the oven flask. Total recovery was 100.34%. Here we found great recovery, but most of the PFOA still remained in the flask and didn't volatilize.

Run #37:

4/17/06

100 ng/mL PFOA was injected at 100 mL/min dry airflow through fused silica. The run was held at 125°C for 24 hrs. There was no HCl wash of the flask. Results showed 9.39 ng/mL in impinger #1, 1.40 ng/mL in impinger #2, 2.18 ng/mL in the XAD resin, and 38.8 ng/mL in the oven flask. Total recovery was 51.77%. There was still poor recovery, but more went through to the impingers than at 100°C.

PFOA Polypropylene Test:

4/19/06

To verify if standards prepared and stored in glass vs. standards prepared and stored in polypropylene made any difference in recoveries, new Free Acid PFOA in H₂O standards were mixed up and placed into polypropylene tubes instead of glass. We compared the new standards with Free Acid PFOA in MeOH standards that were in glass. Results showed virtually no difference in absolute area counts between 10 ng/mL and 100 ng/mL standards that were in polypropylene and glass. It does not appear the PFOA in the standards is adhering to the glass.

Quartz Run #1:

4/19/06

Since there was a concern PFOA was adhering to the sides of our glassware, we wanted to try an all-quartz system instead. A new apparatus was assembled by the 3M glass shop using only 1 impinger. The entire system was now constructed with quartz glass. A thermal desorber was used as the heat source in place of the GC oven. 100 ng/mL Free Acid PFOA in H₂O at 100 mL/min dry air flow was injected through fused silica and held at 150°C for 20 hrs. The temperature recorded by the thermocouple and transfer line only recorded 122°C due to contact gaps on various portions of the thermal desorber. Results showed 1.03 ng/mL PFOA in the impinger, 1.73 ng/mL in the XAD resin, and 72.3 ng/mL in the Quartz flask. Total recovery was 75.06 ng/mL. This is good recovery, but the PFOA is still not migrating to the impinger. At first glance, it appears quartz doesn't help PFOA migrate any better than glass.

Quartz Run #2:

4/25/06

This was a repeat of "Quartz Run #1" except that in this case the GC oven was once again used as the heat source and the thermal desorber was discarded due to the contact gaps. 100 ng/mL Free Acid PFOA in H₂O at 100 mL/min dry air flow was injected through fused silica and held at 150°C for 24 hrs. Results showed 0.954 ng/mL in the impinger, 2.08 ng/mL in the XAD resin, and 27.2 ng/mL in the Quartz flask. Total

recovery was 30.234 ng/mL PFOA. This was poor recovery again, as the PFOA is still not migrating to the impinger. The GC oven will always be used in the future for every subsequent quartz flask run, as this will avoid any possibility of uneven temperature with the flask.

Quartz Run #3:

4/27/06

We wanted to try running a highly concentrated PFOA standard through our all-quartz system. In this run, 1000 ng/mL (or, 1 ppm) Free Acid PFOA in H₂O at 100 mL/min dry air flow was injected through fused silica and held at 150°C for 24 hrs. Results showed 12.2 ng/mL in the impinger, 6.70 ng/mL in the XAD resin, but 269.0 ng/mL in the Quartz flask. Total recovery was 287.9 ng/mL PFOA. Once again there was poor recovery, but at least these values are consistent when comparing them to what would be predicted at this level of PFOA to 100 ng/mL. The quartz flask had about 10X more PFOA remaining in it at 1000 ng/mL than at 100 ng/mL, which would be predicted.

May 2006

PFOA Flask Test 150°C:

5/2/06

We wanted to check on PFOA degradation and PFOA adsorptive losses in quartz flasks vs. glass Erlenmeyer flasks at very high concentrations of PFOA. In this experiment, three 125 mL Erlenmeyer flasks at levels of 100 ng/mL, 1000 ng/mL and 10,000 ng/mL PFOA Free Acid in H₂O were capped and held at 150°C for 24 hrs. A quartz flask with 100 ng/mL PFOA was capped and also held at 150°C for 24 hrs. Results showed <0 ng/mL in the 100 ng/mL flask, 1030 ng/mL in the 1000 ng/mL flask, 660 ng/mL in the 10,000 ng/mL flask, and 54.3 ng/mL in the quartz flask. Since there were so many errors in preparing this experiment, it will be discarded and rerun.

PFOA Flask Test 150°C Rerun:

5/4/06

To test for PFOA adsorptive losses, three 125mL Erlenmeyer flasks were prepared at levels of 100 ng/mL, 1000 ng/mL, and 10,000 ng/mL PFOA Free Acid in H₂O were capped and held at 150°C for 24 hrs. Results showed 32.8 ng/mL PFOA in the 100 ng/mL flask, 242 ng/mL PFOA in the 1000 ng/mL flask, and 7780 ng/mL PFOA in the 10,000 ng/mL flask. It appears that at 10,000 ng/mL, a much better recovery can be obtained. 100 ng/mL and 1000 ng/mL PFOA had similar % recoveries. Results are listed in Table 2. Is there a saturation point at which all active sites are used up on the glassware?

Quartz Run #4:

5/4/06

This run tested rapid injection (1 min.) of PFOA vs. a slower injection (10 min.) to see if variability in injection rates caused any recovery effects. This was a repeat of "Quartz Run #2" except that this time the 100 ng/mL PFOA was injected through the syringe pump at a rate of 100 uL/min (it only took 1 min to completely inject the sample instead of 10 min.). This was done at 100 mL/min dry airflow and was held at 150°C for 24 hrs. Results showed 1.65 ng/mL in the impinger, 1.97 ng/mL in the XAD resin, and 32.7 ng/mL in the quartz flask. Total recovery was 36.32 ng/mL PFOA. It does not appear that injecting PFOA at a faster rate made any significant improvement for recoveries. Results are listed in Table 2.

Quartz Run #5:

5/11/06

We wanted to try using another gas instead of using zero air to move the PFOA,. In this run, 100 ng/mL PFOA Free Acid in H₂O at 100 mL/min dry nitrogen flow was injected through fused silica at the old original pump rate (10 uL/min) and held at 150°C for 24 hrs. This time, nitrogen was used as the flow to see if it would produce better recovery than zero air. Results showed 5.449 ng/mL in the impinger, 1.492 ng/mL in the XAD resin, and 11.817 ng/mL in the quartz flask. Total recovery was 18.758 ng/mL PFOA. It appears that PFOA recovery was worse with nitrogen flow.

Quartz Run #6:

5/15/06

This was an identical repeat of "Quartz Run #5." In this run, 100 ng/mL PFOA Free Acid in H₂O at 100 mL/min dry nitrogen flow was injected through fused silica and held at 150°C for 24 hrs. Results showed 2.707 ng/mL in the impinger, 1.804 ng/mL in the XAD resin, and 2.432 ng/mL in the quartz flask. Total recovery was 6.943 ng/mL PFOA. This run showed worse recovery than even the identical "Quartz Run #5".

Quartz Run #7:

5/16/06

This was a repeat of "Quartz Run #5" except that this time the system was held at 50°C for 24 hrs. Results showed 2.913 ng/mL in the impinger, 0.953 ng/mL in the XAD resin, and 88.703 ng/mL in the quartz flask. Total recovery was 92.569 ng/mL PFOA. This was great recovery, but most PFOA was not transported from the flask.

Quartz Run #8:

5/17/06

We decided our oven flask could have too large of a surface area. This was another repeat of "Quartz Run #5", except this time the system was again held at 50°C for 24 hrs, and an entirely new miniaturized quartz flask apparatus was assembled to hopefully minimize the surface area contact of the glass with the compounds. Results

showed 1.695 ng/mL in the impinger, 2.639 ng/mL in the XAD resin, and 91.794 ng/mL in the quartz flask. Total recovery was 96.128 ng/mL PFOA. This was great recovery, but most of the PFOA was still remaining in the miniaturized flask. From now on, it was decided, that this miniaturized quartz flask assembly would be used.

Cold Finger #1:

5/18/06

A cold finger apparatus was built by the 3M glass shop to see if PFOA could be moved approximately 1-2 inches from a tube inside a thermal desorber up to another glass tube that was kept constantly around -50°C in isopropyl alcohol (IPA) and dry ice. Results showed 37.136 ng/mL PFOA Free Acid in H₂O was successfully moved in the cold finger. Future cold finger experiments will be conducted, as this result seems promising.

Quartz Run #9:

5/22/06

In an attempt to try to use nitrogen to move PFOA one last time, 100 ng/mL Free Acid PFOA in H₂O at 100 mL/min dry nitrogen flow was injected through fused silica and held at 150°C for 24 hrs. The miniaturized quartz flask was used. Results showed 6.082 ng/mL in the impinger, 2.720 ng/mL in the XAD resin, and 15.602 ng/mL in the quartz flask. Total recovery was 24.404 ng/mL PFOA. This was a fair recovery, but it was decided to return to compressed zero air for the flow instead of the nitrogen from this point on.

Quartz Run #10:

5/23/06

We returned to using dry airflow to move PFOA. 100 ng/mL Free Acid PFOA in H₂O at 100 mL/min dry compressed airflow was injected through fused silica and held at 150°C for 24 hrs. The miniaturized quartz flask was used again. Results showed 2.295 ng/mL in the impinger, 2.079 ng/mL in the XAD resin, and 36.914 ng/mL in the quartz flask. Total recovery was 41.288 ng/mL PFOA. There was better overall recovery here compared to using nitrogen flow, but most of the PFOA still remained in the flask. Overall recovery indicated the PFOA might have been decomposing, even at the oven temp used.

Quartz Run #11:

5/24/06

We wanted to reduce the temperature in the oven again. 100 ng/mL Free Acid PFOA in H₂O at 100 mL/min dry compressed air flow was injected through fused silica and held at 50°C for 24 hrs. Results showed 0.749 ng/mL in the impinger, 1.609 ng/mL in the XAD resin, and 133.527 ng/mL in the quartz flask. Total recovery was 135.885

ng/mL PFOA. The expected recovery was overshoot in the flask, but there was still no migration seen here.

Cold Finger #2:

5/25/06

We went back to testing the cold finger apparatus. The same apparatus was used as in "Cold Finger #1". This time, the thermal desorber was kept between 100-120°C. Results showed 8.043 ng/mL was moved and 84.926 ng/mL remained in the bottom of the apparatus. Total recovery was 92.969 ng/mL PFOA. The PFOA didn't migrate well here.

Cold Finger #3:

5/26/06

The same apparatus was used as in "Cold Finger #1", and the thermal desorber was again kept between 100-120°C. Results showed 6.114 ng/mL was moved and 95.031 ng/mL remained in the bottom of the apparatus. Total recovery was 101.145 ng/mL PFOA. The PFOA again didn't migrate well.

PTFE TF 2071 Test:

5/30/06-6/12/06

5/30/06

We decided it was time to complete a standardized run extracting PTFE material (Lot #2071) using the ASE. 12 cells were preconditioned using Method 1 of the ASE. Eight cells were used for a standard curve. Sample A was control PTFE powder that was not run through a 24 hr temperature test. Sample B was powder previously run through the miniaturized quartz flask system at 281°C. Sample C was powder previously run at 150°C. Sample D was powder previously run at 50°C.

50.4 mg of TF2071 powder was weighted out and added to the miniaturized quartz flask at 100 mL/min dry air flow and was held at 150°C for 2 hrs, then at 281°C for 22 hrs. Results were collected in the impinger and XAD resin as before, except this time the powder that remained in the flask was added to a preconditioned cell in the ASE (Sample B). Results showed 51.514 ng/mL in the impinger and 1.906 ng/mL in the XAD resin. Total recovery was 53.42 ng/mL PFOA, or 1.06 ng/mg PFOA.

5/31/06

51.4 mg of TF2071 powder was weighted out and added to the miniaturized quartz flask at 100 mL/min dry air flow and was held at 150°C for 24 hrs. Results were collected in the impinger and XAD resin as before, except this time the powder that remained in the flask was added to a preconditioned cell in the ASE (Sample C). Results showed 9.654 ng/mL in the impinger and 0.314 ng/mL in the XAD resin. Total recovery was 9.968 ng/mL PFOA, or 0.19 ng/mg.

June 2006

6/1/06

49.8 mg of TF2071 powder was weighted out and added to the miniaturized quartz flask at 100mL/min dry air flow and was held at 50°C for 24 hrs. Results were collected in the impinger and XAD resin as before, except this time the powder that remained in the flask was added to a preconditioned cell in the ASE (Sample D). Results showed 4.946 ng/mL PFOA in the impinger and <0 ng/mL in the XAD resin. Total recovery was 4.946 ng/mL PFOA, or 0.10 ng/mg.

50.0 mg of TF2071 powder was weighed out and directly added to a preconditioned cell in the ASE (Sample A) with no prior heating.

6/5/06

The eight standard curve run through the ASE had values ranging from 5-250 ng/mL. 10 uL of 10 ng/uL PFOA IS was added to the standard curve cells and samples A-D prior to the first ASE cycle. 500 uL of C-18 H₂O was added along with the IS, standards, and sample matrix to each respective preconditioned cell.

Sample A and the standards were not preheated to 150°C for 24 hrs as specified. Instead, all 12 cells were run through the ASE using Method 2 as ASE Cycle 1. In future reruns of this experiment, those cells will be preheated to 150°C for 24 hrs as specified to ensure all samples will have been heated for the same time period (24 hrs) prior to run through the ASE.

6/6/06

Sample cells A-D were placed in a GC oven overnight for 24 hrs at 150°C.

The extracted solvent in MeOH from the ASE Cycle 1 produced ~19 mL in each vial. About 6 mL MeOH was added to each vial to bring the total volume to 25 mL in volumetric flasks. 5 mL of these thoroughly mixed solutions were added to 1 mL of Dyneon H₂O (0.5% KOH in 100 mL C-18 H₂O). The MeOH was dried down using a Rapid Vap. 1 mL of 1.0 N Formic Acid and 100 uL of SAS were added to the dried down tubes, which were then vortexed. Each sample was run through SPE. This is the method that is used for all cycles in this experiment.

Results showed 161.138 ng/mL in Sample A (no heating), 723.272 ng/mL in Sample B (heated to 281°C), 188.876 ng/mL in Sample C (heated to 150°C), and 194.470 ng/mL in Sample D (heated to 50°C). So, 3.22 ng/mg was found in Sample A, 14.3 ng/mg was found in Sample B, 3.67 ng/mg was found in Sample C, and 3.91 ng/mg was found in Sample D. It appears that when first heated to 281°C, more PFOA is flushed out of the PTFE material, as only 161.138 ng/mL was found with no prior heating, but 723.272 ng/mL was found at 281°C. However, this result is questionable, as contamination may have been an issue for Sample B.

6/7/06

Sample cells A-D were run through the ASE using Method 2. The cells were then placed in the GC oven overnight for 24 hrs at 150°C.

Cycle 2 through the ASE was run through SPE by the same procedure as in Cycle 1. Results showed 65.11 ng/mL in Sample A, 12.12 ng/mL in Sample B, 35.21 ng/mL in Sample C, and 74.85 ng/mL in Sample D. So, 1.30 ng/mg was found in Sample A, 0.24 ng/mg was found in Sample B, 0.69 ng/mg was found in Sample C, and 1.50 ng/mg was found in Sample D.

6/8/06

Sample cells A-D were run through the ASE using Method 2. The cells were then placed in the GC oven overnight for 24 hrs at 150°C.

Cycle 3 through the ASE was run through SPE by the same procedure as in Cycle 1. Results showed 241.54 ng/mL in Sample A, 17.71 ng/mL in Sample B, 26.25 ng/mL in Sample C, and 24.28 ng/mL in Sample D. So, 4.83 ng/mg was found in Sample A, 0.35 ng/mg was found in Sample B, 0.51 ng/mg was found in Sample C, and 0.49 ng/mg was found in Sample D.

6/9/06

Sample cells A-D were run through the ASE using Method 2.

Cycle 4 through the ASE was run through SPE by the same procedure as in Cycle 1. Results showed 13.01 ng/mL in Sample A, 5.64 ng/mL in Sample B, 10.15 ng/mL in Sample C, and 10.38 ng/mL in Sample D. So, 0.26 ng/mg was found in Sample A, 0.11 ng/mg was found in Sample B, 0.20 ng/mg was found in Sample C, and 0.21 ng/mg was found in Sample D.

6/12/06

Final results were as follows: Sample A (no prior heating) had a total of 9.61 ng/mg. Sample B (heated to 281°C) had a total of 16.06 ng/mg. Sample C (heated to 150°C) had a total of 5.26 ng/mg. Sample D (heated to 50°C) had a total of 6.21 ng/mg. This entire experiment will be repeated, as verification is needed for all these results. It is also believed that during Cycle 1 Sample B became contaminated. Results are shown below in Table 3.

Table 3.
PTFE 2071 Test Results:

	<u>Sample A:</u> (No Preheat)	<u>Sample B:</u> (281°C)	<u>Sample C:</u> (150°C)	<u>Sample D:</u> (50°C)
Initial PTFE levels: (mg added)	50.0 mg	50.4 mg	51.4 mg	49.8 mg
Levels produced by GC oven preheat: (ng/mg PFOA)	N/A	1.06 ng/mg	0.19 ng/mg	0.10 ng/mg
Cycle 1 Results:	3.22 ng/mg	*14.3 ng/mg	3.67 ng/mg	3.91 ng/mg
Cycle 2 Results:	1.30 ng/mg	0.24 ng/mg	0.69 ng/mg	1.50 ng/mg
Cycle 3 Results:	4.83 ng/mg	0.35 ng/mg	0.51 ng/mg	0.49 ng/mg
Cycle 4 Results:	0.26 ng/mg	0.11 ng/mg	0.20 ng/mg	0.21 ng/mg
Final Results: (Total PFOA Levels Found)	9.61 ng/mg	16.06 ng/mg	5.26 ng/mg	6.21 ng/mg

*Note: It is thought that some contamination occurred here for Sample B during Cycle 1.

PTFE TF 2071 Test 2:

6/13/06-6/27/06

6/13/06

We wanted to repeat the first PTFE standardized run on the ASE over again to verify our results. 12 cells were preconditioned using Method 1 of the ASE. Nine cells were used for a standard curve. Sample A was control PTFE powder that was not run through a 24 hr temperature test. Sample B was powder previously run through the miniaturized quartz flask system at 282°C. Sample C was powder previously run at 150°C.

49.4 mg of TF2071 powder was weighted out and added to the miniaturized quartz flask at 100 mL/min dry air flow and was held at 150°C for 2 hrs, then at 281°C for 22 hrs. Results were collected in the impinger and XAD resin as before, except this time the powder that remained in the flask was added to a preconditioned cell in the ASE (Sample B). Results showed 16.693 ng/mL in the impinger and 6.743 ng/mL in the XAD resin. Total recovery was 23.436 ng/mL PFOA.

6/14/06

50.5 mg of TF2071 powder was weighted out and added to the miniaturized quartz flask at 100 mL/min dry air flow and was held at 150°C for 24 hrs. Results were collected in the impinger and XAD resin as before, except this time the powder that remained in the flask was added to a preconditioned cell in the ASE (Sample C). Results showed 38.341 ng/mL in the impinger and <0 ng/mL in the XAD resin. Total recovery was 38.341 ng/mL PFOA.

50.9 mg of TF2071 powder was weighted out and directly added to a preconditioned cell in the ASE (Sample A) with no prior heating.

6/15/06

The nine point standard curve run through the ASE had values ranging from 5-500 ng/mL. 15 uL of 10 ng/uL PFOA IS was added to the standard curve cells and samples A-C prior to the first ASE cycle. 500 uL of C-18 H₂O was added along with the IS, standards, and sample matrix to each respective preconditioned cell.

This time, Sample A and the standards were preheated to 150°C for 24 hrs as specified in a GC oven. All 12 cells were then run through the ASE using Method 2 as ASE Cycle 1.

6/19/06

Sample cells A-C were placed in a GC oven overnight for 24 hrs at 150°C.

The extracted solvent in MeOH from the ASE Cycle 1 produced ~19 mL in each vial. About 6 mL MeOH was added to each vial to bring the total volume to 25 mL in volumetric flasks. These samples were placed in 50 mL polypropylene tubes and capped and held until all subsequent cycles were completed.

6/20/06

Sample cells A-C were run through the ASE using Method 2 as ASE Cycle 2, and the extracted MeOH was placed in polypropylene tubes as in ASE Cycle 1. The cells were then placed in a GC oven overnight for 24 hrs at 150°C.

6/21/06

Sample cells A-C were run through the ASE using Method 2 as ASE Cycle 3, and the extracted MeOH was placed in polypropylene tubes as in ASE Cycle 1. The cells were then placed in a GC oven overnight for 24 hrs at 150°C.

6/22/06

Sample cells A-C were run through the ASE using Method 2 as ASE Cycle 4, and the extracted MeOH was placed in polypropylene tubes as in ASE Cycle 1.

5 mL of all of the thoroughly mixed MeOH solutions in the 50 mL polypropylene tubes were added to 1 mL of Dyneon H₂O (0.5% KOH in 100 mL C-18 H₂O). The MeOH was dried down using a Rapid Vap. 1 mL of 1.0 N Formic Acid and 100 uL of Saturated Ammonium Sulfate were added to the dried down tubes, which were then vortexed. Each sample was run through SPE twice. This is the method of experimentation that was used for all cycles in this experiment.

6/26/06

ASE Cycle 1 results showed 218.952 ng/mL PFOA in Sample A (no heating), 0.00 ng/mL in Sample B (preheated to 282°C), and 26.512 ng/mL in Sample C (preheated to 150°C). So, 4.38 ng/mg PFOA was found in Sample A, 0.00 ng/mg in Sample B and 0.53 ng/mg in Sample C.

ASE Cycle 2 results showed 29.081 ng/mL in Sample A, 0.00 ng/mL in Sample B, and 327.259 ng/mL in Sample C. So, 0.58 ng/mg was found in Sample A, 0.00 ng/mg in Sample B, and 6.55 ng/mg in Sample C.

ASE Cycle 3 results showed 9.537 ng/mL in Sample A, 0.00 ng/mL in Sample B, and 7.572 ng/mL in Sample C. So, 0.19 ng/mg was found in Sample A, 0.00 ng/mg in Sample B, and 0.15 ng/mg in Sample C.

ASE Cycle 4 results showed 0.00 ng/mL in Sample A, 0.00 ng/mL in Sample B, and 13.181 ng/mL in Sample C. So, 0.00 ng/mg was found in Samples A and B, while 0.26 ng/mg was found in Sample C.

6/27/06

Final results were as follows: Sample A (no prior heating) had a total of 5.15 ng/mg. Sample B (heated to 282°C) had a total of 0.47 ng/mg. Sample C (heated to 150°C) had a total of 8.26 ng/mg.

It was interesting how no PFOA was found in Sample B (preheated to 282°C) on this run. Hopefully, this experiment can be repeated a third time to verify if this result was an aberration or not. Also, MeOH will no longer be used to move PTFE material from the miniaturized quartz flask in the oven to the ASE cells because the MeOH is dripping through the bottom of the cell onto the tabletop. There must be another means of scraping PTFE off the sides of the flask to the sand bed of the cell. Results are listed in Table 4.

Table 4.
PTFE 2071 Test 2 Results:

	<u>Sample A:</u> (No Preheat)	<u>Sample B:</u> (282°C)	<u>Sample C:</u> (150°C)
Initial PTFE levels: (mg added)	50.9 mg	49.4 mg	50.5 mg
Levels produced by GC oven preheat: (ng/mg PFOA)	N/A	0.47 ng/mg	0.77 ng/mg
Cycle 1 Results:	4.38 ng/mg	0.00 ng/mg	0.53 ng/mg
Cycle 2 Results:	0.58 ng/mg	0.00 ng/mg	6.55 ng/mg
Cycle 3 Results:	0.19 ng/mg	0.00 ng/mg	0.15 ng/mg
Cycle 4 Results:	0.00 ng/mg	0.00 ng/mg	0.26 ng/mg
Final Results: (Total PFOA Levels Found)	5.15 ng/mg	0.47 ng/mg	8.26 ng/mg

Cold Finger #3b & #4:
6/22/06-6/23/06

A new cold finger apparatus under a vacuum was designed and built by the 3M glass shop. The cold finger base was rinsed with 50% Sulfuric Acid (H₂SO₄), and wiped out with a swab prior to adding PFOA. This apparatus was designed with a larger flask on the top so more IPA and dry ice could keep the samples heated on a hot pad at <-50°C. It was hoped by these experiments that PFOA would be successfully migrated ³/₄ in. to the bottom of the cold finger from the heated flask on the mantle. The heating mantle was kept between 120°C-150°C. Results showed 103.401 ng/mL PFOA was moved to the cold finger successfully during the #3b run, and 111.421 ng/mL PFOA was moved during the #4 run. These are excellent recoveries, so a new similar cold finger apparatus that will hopefully allow airflow to move the PFOA a farther distance will be assembled.

July 2006

Cold Large Finger #1:

7/11/06

A new cold finger with a very large top and surface area for IPA and dry ice to fit into was assembled, and allowed air flow to move from the base up through the top through an XAD resin and out of the system. The temperature of the cold finger was kept at $\sim -70^{\circ}\text{C}$. The temperature of the heating mantle was kept $\sim 100^{\circ}\text{C}$ - 150°C . The goal was to see if 100 ng/mL PFOA could migrate ~ 2 in. to the bottom of the cold finger from the heated flask on the mantle. Results showed 37.7 ng/mL PFOA had reached the cold finger base, and 38.6 ng/mL PFOA was present in the XAD resin. Total recovery was 76.3 ng/mL PFOA. These were very promising results. Therefore, the experiment will be repeated for verification.

Cold Large Finger #2:

7/18/06

This was an identical repeat of "Cold Large Finger #1". Results showed 6.29 ng/mL PFOA had reached the cold finger base, and 33.3 ng/mL PFOA was found in the XAD resin. Total recovery was 39.59 ng/mL PFOA. The XAD resin had similar recovery to the previous run, but not as much PFOA appeared to migrate to the bottom of the cold finger. A reason for that may be due to the large area that must be rinsed on the cold finger with MeOH to use for extraction purposes caused variability in what the true amounts of PFOA present were. The current cold finger design creates a problem with disassembly and rinsing due to a ground glass joint freezing at the junction point between the heated glass and the -80°C cold finger. To separate the glass, one must first remove the IPA / dry ice liquid and CO_2 solid. Secondly, using aqueous to remove the frost build up on the joint, one must attempt to rinse the inside glass before the temperature elevates and the "cold" of the cold finger is lost, the PFOA trapped along with it.

Silanization Run #1:

8/9/06

Since it was hypothesized that active sites on our quartz glassware were preventing the movement of PFOA, a silanizing agent was purchased. It was hoped that this silanizing agent would be able to deactivate any active sites on the glassware. This silanizing agent, called SigmaCote™, was coated onto all glassware used in the GC oven apparatus, including the impinger itself. Then, the glassware was placed into a separate GC oven and heated at 100°C for 1 hr prior to setting up the apparatus as before. 100 ng/mL Free Acid in H_2O PFOA was placed into the miniaturized quartz flask in the GC oven at 100 mL/min dry air flow for 4 hrs and held at 150°C . The results showed 38.176 ng/mL PFOA in the impinger, 3.499 ng/mL in the XAD resin, and 33.628 ng/mL still in the oven flask. Total PFOA recovery was 75.303%. It appears more PFOA was moved during this run than normal, so it was hoped that by repeating the experiment and pre-coating the glassware with SigmaCote™ again, more active sites would be deactivated, which would allow for even better recovery.

Silanization Run #2:

8/14/06

This was a repeat of "Silanization Run #1" exactly. After pre-coating all glassware with SigmaCote™ again, results showed 90.532 ng/mL PFOA in the impinger, and <0 ng/mL in the XAD resin and oven flask. Total recovery was 90.532%. That is excellent recovery, as all of the PFOA recovered successfully moved to the impinger. The experiment will be repeated again for verification.

Silanization Run #3:

8/16/06

This was another repeat of "Silanization Run #1." After pre-coating all glassware with SigmaCote™, results showed 91.544 ng/mL PFOA in the impinger, 1.993 ng/mL PFOA in the XAD resin, and <0 ng/mL PFOA in the oven flask. Total PFOA recovery was 93.537%, all which had been moved successfully. From now on, all glassware used for this study's research will be coated with a silanizing agent such as SigmaCote™.

3M Corporate Toxicology

Analytical Laboratory Bldg 236

To: George Millet

**From: Jeremy Zitzow
Dave Ehresman
Venkateswarlu Pothapragada**

**Study: Annual Report on

Method Development for PFOA Generation Testing from
PTFE**

Date: May/June 2008

Outline

- 1. Introduction**
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 - A. Thermal Degradation Testing / Deactivation of Glassware**
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 - i. Temperature Testing and Movement of PFOA**
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 - B. Accelerated Solvent Extraction (ASE)**
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 - c. Instrument hardware limitation and failures – Oct 2007-Apr 2008**
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 - C. Analysis of PTFE samples using DSC and Photomicrography**
 - a. DSC work found onset @ 325°C**
 - b. Photomicrographs @ 317°C and 297°C**
- 3. Conclusions**

INTRODUCTION

Since the last report, we have focused our efforts on improving the instrumentation and methods dedicated to both the Accelerated Solvent Extraction (ASE) and the thermal degradation studies. The scope of this report will detail challenges faced and problems solved in having these assays meet the requirements set forth in the Enforceable Consent Agreement (ECA) by the EPA. The study goal remains confirmed measurement of PFOA at or below 1 ng/g when spiked into test system components. This proof of concept would then ensure that we could meet the same level of performance when testing PTFE for the generation of PFOA as set forth by the ECA.

EXPERIMENTAL, RESULTS & DISCUSSION

A. Thermal Degradation Testing / Deactivation of Glassware

Over the course of the past year and a half, we have tried both at times successfully and at other times unsuccessfully to move PFOA from our heated reaction vessel to a type of collection system by first deactivating the glassware with various silanating agents. These experiments, though tedious, provided us with a substantial amount of information. However, many variables were involved with figuring out at what temperature, for what duration, and with what concentration of PFOA this could be successfully accomplished. We ran experiments varying the temperature of the reaction vessel, the duration of temperatures once established, and the final temperature of the test process.

The first silanating agent used to silanize the test glassware as constructed by the 3M glass shop was ordered from *Sigma Aldrich, Inc.* SigmaCote was the product tested and initially, it appeared that this would work well at deactivating the glassware. Early experiments with temperature studies tested at 150°C and 200°C, (where the duration of the generation test lasted for 4 hours); produced consistent recoveries of PFOA at or near 90% based on using a single dry impinger kept ~-70°C in a dry ice/IPA bath. We exchanged the dry impinger at ~-70°C with the originally designed dual-impinger system filled with water and an XAD resin placed at the end of the second impinger. This series of impingers and XAD resin was kept in an ice bath at 0°C. Using this multiple impinger train system, we found the overall recoveries improved to near 100%.

The next step was to test the viability of the SigmaCote in the system as the temperature was raised to near 300°C, the predicted onset of the PTFE mixture melting point that we would need to eventually hold for up to 24 hours. It was found that when we placed 50, 100, 150, 200, and 250 ng/g PFOA into the reaction vessel and held the system at 150°C for 2 hours and then at 300°C for 2 hours, we were able to successfully move >90% of the PFOA from the reaction vessel to the two-impinger system. However, once we started adding concentrations of PFOA at greater than 250 ng/g, we found that our overall recoveries dropped significantly to <70%. We also started noticing a solid

buildup of amorphous material was adhering to the sides of our reaction vessel using these elevated temperatures.

We replaced all of our glassware with new glassware and soaked it in an HCl bath overnight prior to the addition of the SigmaCote. This was done in an attempt to remove any impurities and potential deposits of the silanating agent deposited at the required high temperatures required by the test protocol. Further testing indicated that the HCl pretreatment of the glassware was causing complications with the SigmaCote coatings as we found it less and less effective over time. This was indicated by our overall PFOA recoveries of the spiked 250 ng/g trials' being reduced to recovery levels between 22.0-65.6%. The HCl bath was exchanged in favor of a H₂SO₄ bath. However, there appeared to be no real improvement as PFOA was found to recover poorly at only 24.2%. It was decided that we could no longer pretreat our glassware with a strong acid prior to adding silanating agent as it appeared the strong acids were causing the SigmaCote to become less effective at deactivating the glassware when higher temperatures were involved.

We ordered a new lot of SigmaCote, and tried deactivating new glassware. However, at this point, we found that only 58.1-62.5% of our PFOA could be recovered from the impingers. Through further experiments it was determined that SigmaCote had significant lot to lot specific differences which adversely affected recoveries. We were unable to obtain sufficient amounts of the original used lot of SigmaCote and subsequent lots tested failed on recovery testing. It was therefore decided that we would pursue a more reliable silanating agent for this project.

The next set of possible silanating agents we decided to test were 50% mixtures of various acids, including: sulfuric acid, nitric acid, HCl, TFA, triflic acid, and trifluorobutyric acid. Using a heating block, we conducted various tests to see if by pre-rinsing small vials with each of these acids, and then adding 100 ng/g of PFOA, we would hopefully move most of the PFOA out of these vials when kept under similar airflow conditions as to our generation test system. After conducting a series of tests involving all of these compounds, we discovered that vials pre-rinsed with HNO₃ or TFA appeared to be more efficient at moving PFOA.

We ran a series of experiments involving different concentrations of HNO₃ and TFA from 10-50% in strength and found that the weaker acids tended to move the PFOA more effectively, specifically in TFA prerinsed trials. So, we focused on using TFA as a viable silanating agent.

After running a series of experiments testing varying concentrations of TFA, we discovered that 1% TFA seemed to be the most effective at moving PFOA out of small vials into the atmosphere when heated at temperatures between 120-150°C and kept under similar conditions to the generation test system. We ran a series of experiments using 1% TFA as our silanating agent for our generation test glassware, and found that <60.6% of our PFOA was moved from the reaction vessel to the impingers. When we traded the two-impinger ice bath system for a dry ice/IPA impinger system, the results only showed

13.4-32.6% of the PFOA could be moved. It was decided that TFA would not be a viable silanating agent to move PFOA.

Over the course of our testing for viable silanating agents, we evaluated other select compounds. We first tried C9 and C10 carboxylic acids to see if they would preferentially compete for available active sites on the glassware used throughout our entire system (i.e. reaction vessel, transfer lines, impingers). Using these selected carboxylic acids in conjunction with the glassware tested, we found PFOA recoveries at 66.1% and 82.1%, respectively. We abandoned these compounds due to the inability to find pure reference materials that did not contain trace amounts of C8 chemistry, specifically PFOA. We also found these agents did not produce sufficient recoveries to warrant continued use.

We then consulted two experts in silanating materials here at 3M, and were given four different compounds to test for their ability to deactivate the glassware. Unfortunately, none of these compounds proved to be acceptable silanating agents, as less than 50% of the PFOA target value spiked was recovered when running experiments through the generation test.

We met again with the internal 3M experts and investigated the chemistries formulated in SigmaCote. After much discussion, it was decided that we would order the active ingredients in SigmaCote directly from the original manufacturer. Therefore, 1,7-Dichloro-octamethyltetra-siloxane, and 1,5-Dichloro-hexamethyltri-siloxane were ordered directly from *Gelest, Inc.* We ran preliminary tests on these two test compounds using a heating block assembly under controlled temperatures and airflows. The preliminary testing indicated we were able to efficiently remove PFOA from the treated glassware surfaces under controlled conditions of temperature and airflow. Since the 1,5-Dichloro-hexamethyltri-siloxane appeared to be more efficient at moving PFOA in these studies, we initially decided to complete additional testing with this compound as our primary choice for silanating all required glassware for this project (reaction vessels, transfer lines, impingers).

We ran multiple experiments with the 1,5-Dichloro-hexamethyltri-siloxane as our silanating agent over the next few months with very promising results. Temperatures were varied during our experiments from 150-300°C using the thermal generation test apparatus called for in the ECA protocol. The results are listed in Table 1.

It was decided to again try using a dry ice/IPA cold trap to capture the PFOA instead of the two-impinger system. The initial results were promising, as 92.1-110.8% PFOA was recovered. However, maintaining conditions of -80°C overnight for continuous operation was a drawback to this study design. There was concern also that the condensation of the humidity in the tube would restrict airflow and increase the back pressure in the generation test system. Therefore, the two-impinger system advantages of continuous airflow and unattended temperature control over 24 hours led us back to using this system.

In order to continue our generation testing protocol, it became necessary to conduct various “blank runs” (i.e. no PFOA added to the reaction vessel) through the system apparatus to check for background PFOA levels. Initial testing with our thermal generation test apparatus indicated problematic background levels of PFOA. Further testing found the XAD resins contained measurable amounts of PFOA under blank test conditions. A new lot of XAD resins was ordered from Supelco and tested. These new cartridges were found to have much lower PFOA background levels well below the lower limit of quantitation (LLOQ). Based on this finding, all new lots of XAD resins will be tested for background PFOA prior to use.

Isolating the impingers and our reaction vessel, we still experienced measurable PFOA background levels. Therefore, we replaced the activated charcoal filters (located post flow controller prior to the mixing chamber) with new ones to reduce any unwanted PFOA background from our zero air gas supply. After they were replaced, PFOA background levels dropped to manageable levels. The charcoal filters will need to be replaced bi-annually in order to avoid unacceptable background PFOA levels.

We have had continued success in moving spiked standards of PFOA from the reaction vessel to the two-impinger collection system. We have spiked 5, 7.5 and 10 ng/g PFOA into the reaction vessel, and recovered PFOA at levels between 77.4-103.7%. The initial studies on the PTFE-mixed lot, using the ASE, have shown much lower PFOA levels than anticipated. We have transitioned to testing for PFOA at lower spiked levels in the thermal generation test due to the initial findings of the ASE work conducted on the PTFE-mixed lot.

B. Accelerated Solvent Extraction (ASE)

During the period of time when we concentrated our efforts on finding a proper silanating agent for the glassware used in the generation test, the Dionex ASE instrument was not being used. As a result, when the ASE was brought back online, background levels of PFOA were tested and reviewed. The background concentrations of PFOA were of concern at this time, as they were found to be higher than expected.

Our goal was to first find the levels of PFOA present in the PTFE-mixed lot powder given for this project. Running four samples each through four cycles of the ASE showed that the PFOA levels were all <10 ng/g, as our LLOQ was 10 ng/g. Knowing this information, it was decided to test an older lot of PTFE powder that had been run 18 months prior to see if the PFOA levels in that lot were similar to this new mixed lot of PTFE powder. Significant concentrations were found in the previously analyzed lot of PTFE material, thus indicating the instrumentation was working properly. Through additional experiments, however, it was discovered that the ASE was not delivering consistent levels of MeOH solvent through each cycle, and a Dionex field service engineer was brought in to repair the instrument. Therefore, all of the results using the ASE instrument from our recent experiments were put into question. When the repair was completed, we resumed experimentation using the ASE.

The new PTFE-mixed lot powder by ASE was found to have PFOA concentrations at less than 10 ng/g. Therefore, adjustments to the range covered by the standard curve extracted using the ASE had to be reduced to the appropriate levels. Previously, the LLOQ had been established at 10 ng/g. Based on this new information, it was decided to reduce the standard curve range to 0.5-25 ng/g PFOA. The target value of the LLOQ was set at 0.5 ng/g. At these target concentrations, it was discovered that there was excessive background PFOA being contributed by the system itself. Non-linear recoveries were occurring apparently due to system background interference found to be contributed by the system itself at levels higher than our 0.5 ng/g LLOQ. Repeat testing of blank ASE cells through the normal extraction process confirmed high background PFOA concentrations. The range of background concentrations was between 1.27-3.35 ng/g PFOA in blank cells; definitely levels high enough to adversely affect our standard curves and regression data.

We ran a series of experiments changing the standard curve from 5 to 25 ng/g. These higher standard curve targets still remained non-linear and irreproducible. The ASE protocol was changed to not include heating the cells prior to the initial extraction cycle. Standard curves extracted using these changes to the ASE protocol still remained non-linear. Variable amounts of background PFOA contamination from the ASE system itself were suspected. Therefore, all of the PTFE tubing in the instrument was changed to PEEK tubing in an effort to reduce the background levels of PFOA that were suspected of leaching from the PTFE tubing. It was not possible to remove all of the internal tubing and additional blank ASE testing still showed PFOA concentrations from 1.80-3.76 ng/g.

In order to identify other possible sources of PFOA contamination from the ASE, we evaluated various ASE components apart from the automated extraction process to see if any of the components themselves were contributing to the background PFOA concentration. Filters, o-rings, cell frits, cell snap rings and Ottawa sand were tested separately, as were the collection vials for significant contribution of PFOA. We found that none of these parts contributed enough background PFOA to be of concern. It was decided to run another series of blank ASE cells through the cycle process which now showed even higher PFOA levels in the background, ranging from 2.95-9.85 ng/g.

During a conference call, it was suggested that a possible additional source of PFOA was the nitrogen gas and delivery system tubing. We swapped the nitrogen tank with an argon tank and ran another set of blank ASE cells through the extraction process. Extraction results proved the nitrogen tank itself was not the cause of the PFOA background concentration, as the blank cells extracted still showed 1.61-8.63 ng/g of PFOA when extracted using a constant flow of argon.

Ultimately, it was decided to test the nylon tubing that connected the nitrogen tank to the ASE itself for background PFOA. We were surprised to find when we solvent extracted the tubing for PFOA from a 1g section of this tubing, we found 12.8 ng/g of PFOA. We immediately changed this nylon tubing to stainless steel tubing, as it was a concern that the airflow through the tubing was contributing to background PFOA in our

experiments. However, after replacing the nylon line with stainless steel tubing, another set of blank ASE cells still had 2.18-13.2 ng/g PFOA present. By implementing charcoal filters after the flow controllers on the thermal generation testing apparatus led us to install a large, inline activated carbon filter between the nitrogen gas supply device and the ASE instrumentation.

Prior to installing the activated carbon filter, our experiments with the ASE had been based on extractions using 100mg of PTFE material. Since the PFOA levels were found to be lower than anticipated in these PTFE samples, it was decided that we could increase the size of the sample from 100mg to 1g of sample. Therefore, our standard curves would be based on a 1g extraction instead of a 100mg extraction. The combination of the increased PTFE material used and the placement of the activated carbon filters resulted in the extractions of blank ASE cells showing acceptable background levels of PFOA at <0.35 ng/g.

Increasing the amount of PTFE material tested and knowing that instrument PFOA background issues remained, it was decided that the LLOQ should be held to 1.0 ng/g throughout the ASE process as well as with the thermal PFOA generation testing. The capacity of the 5 mL cells on the ASE was reviewed relative to the possibility of using 2g of material. The cells would handle 2g of material, therefore changes were made to our standard curves. These changes to the amount of PTFE extracted using the ASE resulted in changes to the glassware in the thermal generation testing as well.

The reaction vessel previously used in the thermal generation testing apparatus was replaced with a 25 mL Erlenmeyer style flask to increase the surface area for the PTFE to be exposed to the continuous airflow during heating. Initial glassware using the new design had ground glass joints. Raising the temperature to 315°C for 24 hours tended to fuse the glass joint permanently together. A second redesign using polished glass joints fused to a flared base consisting of a 25 mL Erlenmeyer flask resolved this issue. Since it is essential that the flask material be recovered and transferred to the ASE cell for extraction after testing at 315°C for 24 hours, new glassware inventory was built using the polished glass fittings.

C. Analysis of PTFE samples using DSC and Photomicrography

Using the DSC (Differential Scanning Calorimeter), the onset of the melting point of the PTFE-mixed lot powder was found to be in the region of 325°C. This was verified by 4 trials, which found the onset to be 324.98°C, 324.83°C, 324.67°C and 324.62°C. The average onset was 324.78°C. From this information, it was decided that the future experiments would be conducted at 315°C and 295°C, which are 10°C and 30°C less than the onset, as specified in the ECA protocol.

Photomicrographs of the PTFE mixed-lot powders were taken at 317°C and 297°C. The photos can be found in Figure 1.

CONCLUSIONS

In summary, using the changes as presented, we have experienced success with both the ASE and the thermal generation testing methods when applied to PTFE materials for measuring PFOA concentrations present. We have conducted multiple blank testing runs with the ASE equipment where the PFOA concentration measured remain at less than 1.0 ng/g. Multiple extracted blank cells continue to produce acceptable PFOA background levels using the ASE method. ASE extracted standard curves from 0.5 to 17.5 ng/g using nine standards have regression statistics where “R” is >0.9992. Using 2g of PTFE materials in triplicate, we have found low concentrations of PFOA with good precision from the initial extractions. Subsequent extractions, as required in the ECA, have area counts well below the LLOQ for all replicates.

The main improvements to the ASE system were as follows: 1) retrofitting all ASE lines with PEEK tubing where possible; 2) replacing the nylon line from the nitrogen supply tank to the back of the ASE instrument; 3) filtering all nitrogen gas through an activated carbon filter; and 4) increasing the target amount (mass) of PTFE material tested.

The increase in the mass of PTFE material to be tested required increasing the surface area of the heat generation testing vessel. This change then required modification of the overall glassware to polished glass fittings as the temperatures required seized the ground glass fitting post heating once the glassware had been silanized.

The overall proof of transport using PFOA spiked concentrations in both the ASE and the thermal generation testing apparatus was required to validate the testing of the PTFE samples. If the PFOA concentrations were not recoverable under these established test conditions, then testing the PTFE material itself for the presence of and potential generation of PFOA under the identified conditions of heat, humidity and airflow would not be valid. Mass balance of the PFOA concentrations suspected of being in or produced by the PTFE material can then be confirmed based on pre- and post-PFOA measurement of PFOA concentrations using accelerated solvent extraction (ASE) methods as described. The ASE process was further validated using both PFOA standards and stable $^{13}\text{C}_2$ labeled PFOA internal standards. The internal standards were extracted through the initial ASE instrument cycle for all standards, blanks and unknowns. Exhaustive re-extraction cycles using the ASE method show the residual PFOA remaining in the PTFE materials as tested continues to decrease in concentration below the LLOQ on each successive instrument cycle. Post heating extractions of the reaction vessel show no measurable PFOA concentrations remain in the reaction vessel as well.

In conclusion, the single most important task to date has been finding an acceptable silanating agent capable of deactivating glass so that low concentrations of PFOA can be moved reliably under controlled conditions of temperature and airflow from a reaction vessel to a collection system.

Appendices

Table 1: Effect of Temperature on Stability/Decomposition of PFOA using 1,5-Dichloro-hexamethyltri-siloxane

Figure 1: Photomicrographs of PTFE material at 317°C and 297°C

Experimental Log: Data and Results: See attached.

