EMISSIONS OF FLUORINATED COMPOUNDS FROM THE COMBUSTION OF CARPETING

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ABSTRACT

One of the emerging waste streams that will likely be disposed of in combustors is carpet, due to its high heating value and combustibility. Some of the stain-resistant coatings that carpeting is treated with contain perfluorinated compounds (PFCs) such as perfluorocation cacid (PFOA) and their corresponding homologues ($C_6 - C_{14}$ acids) as well as fluorotelomer alcohols and fluoropolymers. PFOA has recently been implicated as a chemical of concern due to its toxicity. It is unknown as to whether PFCs can be released from combustion, or formed as by-products in combustors. This paper reports on a study in a 0.73 kW pilot-scale rotary kiln incinerator simulator to qualitatively and, where applicable; quantitatively assess the potential for emissions of fluorinated compounds from combustion devices. In this study, a limited number of PFCs were found in trace levels in the stack, and the concentrations were relatively independent of kiln feed, suggesting that PFCs are effectively destroyed even under mild combustion conditions, and the trace levels that were found were due to either trace contamination of the sampling duct with fluorinated compounds due to historical use of Teflon and other fluorpolymers, or sampling artifacts.

INTRODUCTION

When a building or outdoor area that was contaminated with biological/chemical agents or toxic industrial chemicals, and is decontaminated and restored, a significant amount of the resulting residues may be disposed of through thermal incineration. Common building materials have typically never been assessed as combustion fuels; the materials removed from decontamination activities may not normally be fed in large quantities to incinerators, and so research must be performed to assess the combustion of common building materials when used as fuel in a combustion system. One of the main waste streams that will be disposed of in combustors includes carpet, due to its high heating value, and combustibility. Cement kilns, in particular, provide a good potential application for carpeting as a supplemental fuel (1).

Carpeting can be treated with stain resistant coatings. Some of these stain-resistant coatings contain perfluorinated compounds (PFCs) such as perfluorooctanoic acid (PFOA) and their corresponding homologues ($C_6 - C_{14}$ acids) as well as fluorotelomer alcohols and fluoropolymers. PFOA has recently been implicated as a chemical of concern due to its toxicity (2, 3, 4, 5, 6, 7). It is unknown as to whether PFCs can be released from combustion, or formed as by-products in combustors. Ellis et al. 2002 (8) suggest that thermolysis of fluoropolymers may be a source of halogenated organic acids in the environment.

The primary goal of this study was to assess whether PFCs can be released from combustion facilities burning carpeting.

EXPERIMENTAL

The experiments were performed on the EPA's Rotary Kiln Incinerator Simulator (RKIS) facility located in Research Triangle Park, NC. The RKIS has been described in detail elsewhere (9) and consists of a 0.73 kW (250,000 Btu/hr) primary combustion chamber followed by a 0.73 kW (250,000 Btu/hr) secondary combustion chamber. Both the primary and secondary combustion chambers are fired by natural gas. For these tests, the burner in the secondary combustion chamber was off. Fig. 1 shows the RKIS.



Fig. 1. EPA Rotary Kiln Incinerator Simulator

The approach to this study was to select a set of nominal operating conditions for the RKIS facility, representing a relatively mild (i.e., temperatures < 1000 °C and the secondary combustion chamber off) combustor operation, and manually feed a fixed size charge of carpeting into the RKIS over a period of time, where Continuous Emissions Monitors (CEMs) were used to measure the concentrations of fixed combustion gases and extractive organic sampling methods were used to assess the concentration of PFCs and other fluorinated compounds in the stack.

Testing was performed using two different types of carpeting: one type that contained no stain-resistant treatment, and one type treated with a stain resistant material that contains PFCs.

The test conditions are shown in Table I. The RKIS (with the main burner on and the secondary burner off) was manually charged with 0.454 kg (1 lb) bundles, 1 bundle every 10 minutes, for a 3-hour run duration. This translates to a 2.7 kg/hr (6 lb/hr) feed rate. Since the PFC emission levels were unknown, it was desired that destruction efficiencies (DEs) of at least 99.99% be quantified based on concentrations rather than based on the detection limits. It is estimated that there may be between 0.2 to 2 mg of PFC present per kg of carpet (10). If it is assumed that there will be 99.99% DE of the PFC in the RKIS, 750 pg will be present in the sample train from a 1 hour run (feeding approximately 2.7 kg [6 lb] of carpeting). This is approximately the same as the instrument detection limit. Therefore, based on reasonable assumptions of DE and likely detection limits it was hypothesized that no PFC emissions might be

detected. In case of this occurrence, an additional test was performed where a commercially available PFC-containing material (Zonyl®) was directly doped onto the carpet in the hopes that sufficient material would be introduced into the RKIS to allow >99.99 % DE be quantified based on concentrations greater than the detection limit. Carpet bundles were spiked by diluting 8.82 g of Zonyl into a 100 ml volumetric flask and diluting with methanol. The 18 un-spiked bundles used in Run 6 were placed into a fume hood for spiking and drying. Each bundle was spiked with 5 ml of the 88 mg/ml spiking solution for a total of 440 mg per bundle. Spiking was performed by pipetting the solution across the top face of the carpet bundle. The spiking solution was observed to wick into the carpet bundles for uniform distribution. The carpet samples were allowed to dry for 30 minutes to allow the methanol to evaporate. Two replicate runs were performed on both treated carpet and untreated carpet, and a single combustion blank and a single Zonyl-doped carpet run were performed.

Run	1	2	3	4	5	6
	NA					Zonyl
	(Comb.	Untreated	Treated	Treated	Untreated	Doped
Feed	Blank)	Carpet	Carpet	Carpet	Carpet	Carpet
Run Time (min)	180	145	180	210	140	180
Carpet Fed (kg)	0.0	6.8	7.9	8.8	6.4	8.7
Avg. Carpet Feed Rate (kg/hr)	0.0	2.8	2.6	2.5	2.7	2.9
Avg. O2 [%]	14.0	12.6	12.2	12.1	11.7	12.1
Avg. CO2 [%]	3.5	4.6	4.7	4.7	4.8	4.8
Avg. CO [ppm]	23	60	83	85	113	82
Avg. NOx [ppm]	25	53	52	43	38	61
Avg. THC [ppm]	2	3	3	3	6	1
Avg. Kiln T [°C]	869	952	980	976	998	986
Avg. SCC Mix T [°C]	472	521	536	532	542	534
Avg. SCC Mid T [°C]	524	575	592	593	607	601
Avg. SCC Exit T [°C]	490	542	558	562	575	571
Avg. Duct 1 T [°C]	396	434	445	447	456	457
Avg. Duct 3 T [°C]	311	339	347	348	354	357
Avg. Duct 4 T [°C]	300	327	334	334	339	342
Avg. Duct 5 T [°C]	282	307	313	314	319	322

Table I. Test Conditions

Measurement of PFCs from combustors has never been done before. As such, there are no validated EPA methods. Therefore, several modifications to standard EPA sampling methods were used, as well as an innovative emerging sampling method (AMstack, with a version of Optizorb absorbent resin designed specifically for PFOA/PFOS collection) (11) to attempt a qualitative assessment of PFCs in stack gases. The sample probe used was a standard Modified Method 5 (MM5) (12) sample probe. The sampling was not performed isokinetically, since the analytes of interest were generally gas-phase species only. The collection media downstream of the probe varied. The samples that were simultaneously collected and analyzed included:

- 1) MM5 Probe/methanol impinger samples (n=6)
- 2) MM5 Probe/XAD extract samples (n=6)
- 3) MM5 Probe/Water impinger samples (n=19, combined into 6 runs) [downstream of XAD cartridge)
- 4) MM5 Probe/Tenax extracts (n=6)

5) AMstack Samples (n=6)

Methanolic extracts and impinger samples

Methanolic extracts of XAD and methanolic impinger samples were reduced in volume to 10 mL prior to analysis. All samples were then centrifuged for 5 minutes at 5000 rpm to pelletize particulate matter. An aliquot of methanolic samples (1.0 mL) was passed through a 0.45 μ m nylon centrifuge filter to remove particulate matter. The sample methanol passing the filter was combined with 2mM ammonium acetate (50:50) to give a concentration of the internal standard (IS) ($^{13}C_2$ -PFOA) at 20 ng/ml. A standard curve including a method blank and 0.5, 1. 3. 5, 10 and 25 ng/ml of all analyzed PFCs was constructed as well. Standards were treated as unknowns in all aspects. Standard curves were constructed for each individual PFC by plotting the analyte/IS area on the y axis vs. analyte concentration/IS concentration on the x-axis with 1/x weighting. All standards curves had r > 0.999. The Lower Limit of Quantitation (LLOQ) for each compound was 0.5 ng/mL. Since only 1 or 10 mL was analyzed for the these samples, final numbers will need to be multiplied by 10 to get the total PFC content of the whole methanolic solution. The results section below gives the value in one ml and the total ng in the entire methanolic impinger sample or XAD extract.

Water impinger samples

Solid Phase Extraction (SPE) HLB (60 mg) columns from Waters were preconditioned with 5 ml of methanol and 5 ml of DI water. Each column then received 20 ng of 13C2-PFOA and was loaded with 3 ml of DI water. Next each vessel in its entirely was added to the SPE column via vacuum manifold and funnel adapters. Some samples contained large amounts of particulate matter that clogged the SPE column and not all was able to pass through, making quantitation difficult for these samples. Next the SPE columns were centrifuged to remove residual water and eluted with 4.0 ml of methanol (2 ml; 2x). Next 0.5 ml of elution methanol was centrifuged at 12,000 rpm for 10 minutes to pelletize particulate matter. An aliquot of the supernatant was combined with 2 mM ammonium acetate (50:50) for LC/MS-MS analysis. A standard curve was constructed by adding 0.5, 1, 2, and 5 ng of all PFC to a tube with 20 ng 13C-PFOA and 18O-PFOS and 4 ml of methanol. Standards were otherwise treated as unknowns in preparation.

Tenax extracts

Prior to analysis 2 Tenax tubes were utilized for some methods development. One tube was spiked with internal standards, and one with internal standards plus the PFCs to be analyzed for. Replicate quantities of IS and PFC of interests were spiked into polypropylene receiving vessels. Tenax tubes were eluted with methanol, first with 10 ml, then 5 ml, followed by forced aeration. Quantities based on area counts for IS and PFCs were compared between Tenax spiked samples and spiked samples for calculations of recovery. Recoveries ranged from 86.5 % (PFHS) to 104.2 % (180-PFOS), and were deemed adequate for analysis of Tenax for PFCs. Each Tenax tube was spiked with 50 ng 13C-PFOA/180-PFOS at the top of the Tenax column. Tubes were then gravimetrically eluted with 10.0 ml methanol, followed by 5.0 ml methanol. After gravimetric dripping had ceased, forced aeration was applied until no methanol was recovered. Of the 15 mL applied 10.5 to 12.0 ml was recovered. A sample aliquot of the methanolic extract (0.2 ml) was combined with 2mM ammonium acetate (50:50) for LC-MS/MS analysis. A standard curve was constructed by adding 10, 20, 50 and 100 ng of all PFCs and 50 ng 13C-PFOA/180-PFOS to a tube then adding 15 mL of methanol. Standards were treated as unknowns otherwise.

AMstack Samples

The AMstack sampling system utilized an unheated, borosilicate glass sampling probe, glass absorbent module, with 316L stainless mesh support frits to contain the absorbent resin. This is followed by a series of chilled impingers to remove moisture prior to the metering console. Two sections of resin were used, one with 15 to 20 grams of resin, the second with 5 grams of resin for breakthrough verifications. The second section of resin is also treated with a proprietary, chemically bonded color indicator determined to be non-reactive to the target compounds. This indicator also is permanently bonded into the Optizorb resin, so it is not extractable during sample preparations. The color indicating resin was incorporated into this test series to verify presence/absence of two conditions that may affect PFC collection efficiencies, namely overheating at the resin cartridge, and pH conditions that could affect the capture of the target compounds. During this test series, excessive absorbent heating that could cause resin degradation, and neutral to basic stack gas conditions that could lower the capture efficiency, were not found. This indicates the sample integrity was likely not compromised by any adverse sampling conditions.

HPLC MS/MS analysis

All samples with the exception of the AMstack were analyzed by EPA's National Exposure Research Laboratory (NERL) via HPLC/MS/MS. The AMstack samples were analyzed by AXYS Laboratories (Sydney, B.C., Canada). The NERL-analyzed samples were prepared so as the final solution to be analyzed consisted of 50:50 2 mM ammonium acetate: methanol. A sample volume (10 μ l) was injected into a mobile phase or 23:77 2mM ammonium acetate: Methanol flowing at 200 μ l/minutes. Analytes were resolved chromatographically using a Waters Sunfire C8 column (50 x 3 mm) 5 um particle size. Multiple Reaction Monitoring (MRM) was done for each individual PFC of interest. The area ratio of the analyte to the corresponding IS was taken for quantitation. Standard curves were constructed where necessary, and analyte concentrations were based on generated standard curves for that day. Double blanks and method blanks were run with each assay to assess if systematic contamination was occurring.

The AMstack samples were spiked with isotopically-labeled surrogate standards, diluted with reagent water, cleaned up on SPE cartridges and analyzed by liquid chromatography/mass spectrometry (LC-MS/MS). Up to 100 mL of methanol were diluted to 1 L with reagent water. The sample was applied to a Waters Oasis WAX SPE cartridge and then eluted with 2 mL of basic methanol. An aliquot of recovery standard was added and the volume adjusted to 4 mL in preparation for LC/MS/MS analysis. Final sample concentrations were determined by isotope dilution/internal standard quantification against matrix matched calibration standards carried through the analysis procedure alongside the samples. Detection limits were in the 0.5 - 0.8 ng range.

Target Analytes

Since PFCs had not been measured in combustion samples before, selection of a list of target analytes was constrained by availability of standards. Table II shows the list of target analytes used in this study. The samples analyzed by AXYS had a few additional analytes.

Compound	Acronym	Structure	MW
Perfluorobutanoic acid	PFBA	r H Kan	214
Perfluoropentanoic acid	PFPeA	r H H Ka	264
Perfluorohexanoic acid	PFHxA		314
Perfluoroheptanoic acid	PFHpA	r-	364
Perfluorooctanoic acid	PFOA	r + + + + + + Kon	414
Perfluorononanoic acid	PFNA	r + + + + + + + + + + + + + + + + + + +	464
Perfluorodecanoic acid	PFDA	r	514
Perfluoroundecanoic acid	PFUnA		564
Perfluorododecanoic acid	PFDoA		614
Perfluorobutane sulfonate	PFBS	r + + + + + + =	299
Perfluorohexane sulfonate	PBHxS		399
Perfluorooctane sulfonate	PFOS		499
Perfluorodecane sulfonate	PFDS		599
Perfluorooctane sulfonamide	PFOSA		499

Table II. List of Target Analytes

RESULTS

Analysis of Carpet by X-Ray Fluorescence

The carpet samples were subjected to X-Ray fluorescence (results shown in Table III). The carpet fiber and backing were analyzed separately (3 samples each) and then the results were averaged into a composite result. The fiber samples were evaluated as oxides, with the unaccounted-for mass assumed to be Nylon-6. The backing samples were evaluated as oxides and CO₂, and the unaccounted-for mass assumed to be cellulose. Fluorine was found in all the carpet samples, including those that were supposedly not treated with stain resistant coatings. It is unknown why this was observed, but since XRF is an elemental analysis, the F may not have been from stain-resistant coatings.

	Carpet Fiber		Carpet Backing			
	Treated	Untreated		Treated	Untreated	
Element	Composite	Composite	Element	Composite	Composite	
F	0.289	0.175	Na	0.486	0.331	
Na	0.024	0.012	Mg	2.093	0.312	
Mg	0.013	0.005	Al	0.239	0.085	
Si	0.004	0.006	Si	0.376	0.199	
P		0.007	P	0.114	0.037	
I	0.053	0.007	S S	0.089	0.092	
	0.005	0.071	Cl	0.009	0.010	
	0.003	0.004	K	0.078	0.036	
<u> </u>		0.009	Ca	8.12	9.31	
Ca	0.032	0.046	Ti	0.018	0.004	
Ti	0.004	0.077	Mn	0.012	0.002	
Mn		0.002	Fe	0.172	0.035	
Fe	0.005	0.004	Ni	0.004	0.004	
Ni	0.004	0.004	Sr	0.007	0.018	
Sr	0.002	0.011	0	5.81	4.55	
Ba		0.019	CO2	12.69	10.77	
0	0.122	0.190	Cellulose	69.68	74.20	
Nylon 6	99.43	99.45	1			

 Table III. XRF Analytical Results (mass %)

Methanolic XAD extracts and Methanolic impinger samples

Table IV lists the PFCs found in the methanol impingers. Most compounds were either not detected or below the limits of quantitation. The only PFC that was consistently found in the samples was PFHxA, and there was not a statistically significant difference between the results from all the runs, including Run 6 which had doped large quantities of Zonyl® into the carpet. These results suggest that any PFCs that we are measuring are not likely due to any PFCs that were present in the carpet that was fed into the RKIS. There is also the possibility that the PFCs aren't getting trapped by the sampling media; although a wide range of potential methods were used to acquire the sample, the entire universe of options was not explored.

One possible explanation is that the nearly ubiquitous use of Teflon and other fluoropolymers on the RKIS ducting (in the form of Teflon tape and sampling line) has resulted in trace contamination of the sampling duct with low levels of PFCs. Another possible explanation is that in spite of best efforts to minimize use of Teflon in all aspects of sampling for these tests, some residual Teflon may have contacted the sampling equipment or may have been used in the manufacturing process of the solvents, sampling, or analytical equipment, resulting in artifacts.

Run	1 (Comb. Blank)	2 (Untreated Carpet)	3 (Treated Carpet)	4 (Treated Carpet)	5 (Untreated Carpet)	6 (Zonyl- doped Carpet)
Compound	ng/m3	ng/m3	ng/m3	ng/m3	ng/m3	ng/m3
PFDoA	ND	ND	ND	<loq< th=""><th>ND</th><th>ND</th></loq<>	ND	ND
PFUA	ND	<loq< th=""><th><loq< th=""><th><loq< th=""><th>ND</th><th>ND</th></loq<></th></loq<></th></loq<>	<loq< th=""><th><loq< th=""><th>ND</th><th>ND</th></loq<></th></loq<>	<loq< th=""><th>ND</th><th>ND</th></loq<>	ND	ND
PFDA	<loq< th=""><th><loq< th=""><th><loq< th=""><th><loq< th=""><th>ND</th><th><loq< th=""></loq<></th></loq<></th></loq<></th></loq<></th></loq<>	<loq< th=""><th><loq< th=""><th><loq< th=""><th>ND</th><th><loq< th=""></loq<></th></loq<></th></loq<></th></loq<>	<loq< th=""><th><loq< th=""><th>ND</th><th><loq< th=""></loq<></th></loq<></th></loq<>	<loq< th=""><th>ND</th><th><loq< th=""></loq<></th></loq<>	ND	<loq< th=""></loq<>
PFNA	<loq< th=""><th><loq< th=""><th><loq< th=""><th><loq< th=""><th>ND</th><th>ND</th></loq<></th></loq<></th></loq<></th></loq<>	<loq< th=""><th><loq< th=""><th><loq< th=""><th>ND</th><th>ND</th></loq<></th></loq<></th></loq<>	<loq< th=""><th><loq< th=""><th>ND</th><th>ND</th></loq<></th></loq<>	<loq< th=""><th>ND</th><th>ND</th></loq<>	ND	ND
PFOA	<loq< th=""><th>564</th><th>135</th><th><loq< th=""><th><loq< th=""><th>33.4</th></loq<></th></loq<></th></loq<>	564	135	<loq< th=""><th><loq< th=""><th>33.4</th></loq<></th></loq<>	<loq< th=""><th>33.4</th></loq<>	33.4
PFHpA	<loq< th=""><th><loq< th=""><th><loq< th=""><th><loq< th=""><th><loq< th=""><th><loq< th=""></loq<></th></loq<></th></loq<></th></loq<></th></loq<></th></loq<>	<loq< th=""><th><loq< th=""><th><loq< th=""><th><loq< th=""><th><loq< th=""></loq<></th></loq<></th></loq<></th></loq<></th></loq<>	<loq< th=""><th><loq< th=""><th><loq< th=""><th><loq< th=""></loq<></th></loq<></th></loq<></th></loq<>	<loq< th=""><th><loq< th=""><th><loq< th=""></loq<></th></loq<></th></loq<>	<loq< th=""><th><loq< th=""></loq<></th></loq<>	<loq< th=""></loq<>
PFHxA	28.1	50.7	53.8	58.7	25.0	47.7
PFOS	ND	<loq< th=""><th>ND</th><th>ND</th><th>ND</th><th>ND</th></loq<>	ND	ND	ND	ND
PFHS	ND	ND	ND	ND	ND	ND
PFBS	ND	ND	<loq< th=""><th>ND</th><th>ND</th><th>ND</th></loq<>	ND	ND	ND

Table IV. PFCs in Methanol Impingers

< LOQ = detected but below limit of quantitation

ND = not detected

XAD extract Methanol

The XAD extracts of the MM5 sampling train yielded similar results, shown in Table V. Trace, quantifiable levels of PFNA, PFOA, PFHpA, and PFHxA, as well as extremely low levels of PFOS were found in the XAD, including Run 1 (the combustion blank). It must be noted that the sampling train with the XAD module included the water impingers downstream, so the two sample fractions must be combined to estimate the total PFC emissions.

		2			5	6 (Tonyl
		4			5	o (Zonyi-
	1 (Comb.	(Untreated	3 (Treated	4 (Treated	(Untreated	doped
Run	Blank)	Carpet)	Carpet)	Carpet)	Carpet)	Carpet)
Compound	ng/m3	ng/m3	ng/m3	ng/m3	ng/m3	ng/m3
PFDoA	ND	ND	ND	ND	ND	ND
PFUA	ND	ND	ND	ND	ND	ND
PFDA	ND	ND	ND	ND	ND	ND
PFNA	<loq< th=""><th>2.7</th><th><loq< th=""><th>ND</th><th><loq< th=""><th>1.2</th></loq<></th></loq<></th></loq<>	2.7	<loq< th=""><th>ND</th><th><loq< th=""><th>1.2</th></loq<></th></loq<>	ND	<loq< th=""><th>1.2</th></loq<>	1.2
PFOA	6.8	11.9	4.5	5.2	5.5	5.2
PFHpA	3.9	6.9	2.9	2.7	3.8	3.5
PFHxA	6.2	13.1	5.5	5.0	8.0	6.6
PFOS	ND	<loq< th=""><th><loq< th=""><th><loq< th=""><th><loq< th=""><th><loq< th=""></loq<></th></loq<></th></loq<></th></loq<></th></loq<>	<loq< th=""><th><loq< th=""><th><loq< th=""><th><loq< th=""></loq<></th></loq<></th></loq<></th></loq<>	<loq< th=""><th><loq< th=""><th><loq< th=""></loq<></th></loq<></th></loq<>	<loq< th=""><th><loq< th=""></loq<></th></loq<>	<loq< th=""></loq<>
PFHS	ND	ND	ND	ND	ND	ND
PFBS	ND	ND	ND	ND	ND	ND

Table V. PFCs in XAD Methanol Extracts

< LOQ = detected but below limit of quantitation

ND = not detected

Water Impinger Samples

The results from the analysis of the water impingers are shown in Table VI. Note that all compounds were analyzed for in the water impingers, but only PFHxA, PFHpA and PFOA were found to be above the LOQ = 0.5 ng total in sample. Therefore only those data are shown.

		2		-	5	6 (Zonyl-
	1 (Comb. Blank)	(Untreated	3 (Treated	4 (Treated	(Untreated	doped Cornet)
		Carper)	Carper)	Carper)	Carper)	Carper)
Compound	ng/m3	ng/m3	ng/m3	ng/m3	ng/m3	ng/m3
PFOA	0.4	0.5	0.3	0.3	<loq< th=""><th>0.9</th></loq<>	0.9
PFHpA	0.5	0.4	0.3	0.1	<loq< th=""><th>0.1</th></loq<>	0.1
PFHxA	0.6	0.2	0.2	0.5	0.3	0.8

Table VI. PFCs in Water Impingers

< LOQ = detected but below limit of quantitation

ND = not detected

Tenax Methanol Extracts

The results from the Tenax methanol extracts are shown in Table VII. There was nothing quantified in any of those samples, and only a handful of compounds were even detected. This observation suggests that Tenax is not a very effective sorbent media for collection of very low levels of PFCs.

		2			5	6 (Zonyl-
	1 (Comb.	(Untreated	3 (Treated	4 (Treated	(Untreated	doped
Run	Blank)	Carpet)	Carpet)	Carpet)	Carpet)	Carpet)
Compound	ng/m3	ng/m3	ng/m3	ng/m3	ng/m3	ng/m3
PFDoA	ND	ND	ND	ND	ND	ND
PFUA	ND	ND	ND	ND	ND	ND
PFDA	ND	ND	ND	ND	ND	ND
PFNA	ND	ND	ND	ND	ND	ND
PFOA	ND	ND	ND	ND	ND	ND
PFHpA	ND	ND	ND	ND	ND	ND
PFHxA	ND	ND	ND	<loq< th=""><th>ND</th><th>ND</th></loq<>	ND	ND
PFOS	ND	<loq< th=""><th><loq< th=""><th>ND</th><th>ND</th><th>ND</th></loq<></th></loq<>	<loq< th=""><th>ND</th><th>ND</th><th>ND</th></loq<>	ND	ND	ND
PFHS	ND	ND	ND	ND	ND	ND
PFBS	ND	ND	ND	ND	ND	ND

Table VII. PFCs in Tenax Methanol Extracts

< LOQ = detected but below limit of quantitation

ND = not detected

AMstack Extracts

The AMstack sample results, shown in Table VIII showed very trace levels of a similar set of PFCs, with the addition of seeing measurable quantities of the sulfur-containing species. This suggests that the sorbent used in the AMstack may be more effective at collecting the sulfur-containing PFCs, a goal in the original development of the resin used in this study. Again, as was shown in all the other samples, levels during the combustion blank were not significantly different than the levels during carpet combustion tests.

	14010 11			~		
		2			5	6 (Zonyl-
	1 (Comb.	(Untreated	3 (Treated	4 (Treated	(Untreated	doped
Run	Blank)	Carpet)	Carpet)	Carpet)	Carpet)	Carpet)
Compound	ng/m3	ng/m3	ng/m3	ng/m3	ng/m3	ng/m3
PFBA	ND	ND	ND	ND	ND	ND
PFPeA	ND	ND	ND	ND	ND	ND
PFHxA	0.2	0.3	0.3	0.2	0.5	0.8
PFHpA	ND	ND	0.2	ND	ND	0.3
PFOA	0.5	1.0	1.3	1.3	2.2	2.0
PFNA	ND	ND	ND	ND	ND	ND
PFDA	ND	ND	ND	0.2	ND	0.5
PFUA	ND	ND	ND	ND	ND	ND
PFDoA	ND	ND	ND	ND	ND	0.3
PFBS	ND	ND	ND	ND	ND	ND
PFHS	ND	ND	ND	ND	ND	ND
PFOS	0.6	1.6	1.5	1.6	3.3	3.4
PFOSA	0.3	0.3	0.6	0.4	0.9	0.4
PFDS	ND	ND	ND	3.5	3.0	3.8

Table VIII. PFCs from AMstack Sampling Train

< LOQ = detected but below limit of quantitation

ND = not detected

Summary of Sampling Method Effectiveness

Fig. 2 shows a grid of which sample techniques caught which species. The Tenax clearly did not catch any of the target analytes. The methanol impingers seemed to catch the greatest diversity of the acids, but did not catch any of the sulfur-containing compounds. The AMstack was able to catch the sulfur-containing target analytes. It must be noted that the water impingers were downstream of the XAD trap, so only the materials that broke through the XAD were caught in the water impingers.

Fig. 3 shows a subset of the data, showing the concentrations of the Hexa- and Octa- substituted PFC concentrations as a function of sampling technique. Again, clearly the Tenax did not catch any of these particular targets. The combined total for the XAD and the water impingers appears to be approximately the same as the results for the methanol impingers, suggesting that similar amounts of those compounds were caught in the XAD and water impingers compared to the methanol impingers. However, looking at Fig. 2, some compounds that were caught in the methanol impingers were not caught at all in the XAD/water impinger train.

	Quantified in at	least half the	1		
	Detected at LOC) in at least ha	s 🛛 →		
	Not Detected in	at least half th	\downarrow		
	Not Analyzed for	or		?	
PFBA	?	?	?	?	Ļ
PFPeA	?	?	?	?	↓
PFHxA	\uparrow	\uparrow	1		1
PFHpA	\rightarrow	\uparrow	1	\rightarrow	\downarrow
PFOA	\uparrow	↑	1	\downarrow	1
PFNA	\rightarrow	\rightarrow	Ļ	\downarrow	\downarrow
PFDA	\rightarrow	Ļ	\downarrow	\downarrow	\downarrow
PFUA	\rightarrow	Ļ	\downarrow	Ļ	Ļ
PFDoA	↓	Ļ	Ļ	Ļ	Ļ
PFBS	↓	Ļ	\downarrow	Ļ	Ļ
PFHS	↓	Ļ	Ļ	Ļ	Ļ
PFOS	↓	\rightarrow	\downarrow	Ļ	1
PFOSA	?	?	?	?	1
PFDS	?	?	?	?	1
	MM5	MM5	MM5	MM5	
	Probe/	Probe/	Probe/	Probe/	
	methanol		Water	Tenax	
	impinger	extract	impinger	extracts	AMIstack

Fig. 2. Matrix of Ability of Sampling to Capture Different Species



Fig. 3. Concentrations of PFOA and PFHxA in Different Samples

CONCLUSIONS

Experiments were performed in a pilot-scale rotary kiln incinerator simulator, in an effort to quantify levels of PFCs emitted during combustion of carpet. Levels were compared during operation on natural gas alone, with treated and untreated carpet materials, and with carpeting deliberately doped with high concentrations of a commercially available PFC mixture. Since the PFC collection effectiveness of conventional sampling approaches was not known, several variations were attempted, in an effort to assure that if PFCs were being emitted, that they would be collected.

In all cases, most PFCs were either not detected or were at such low concentrations to not be quantifiable. PFHxA and PFOA were the most consistently detected species, and all were at levels well below 1 μ g/m3. In addition, there was not a statistically significant difference between PFC levels while only burning natural gas and while burning carpet (even the carpet doped with large quantities of PFCs. This suggests that PFCs are effectively destroyed in combustors, even under relatively mild conditions, and that trace PFCs detected during sampling activities are either contaminants in the sampling duct (perhaps due to use of Teflon tape or other Teflon components) or else artifacts of the sampling/analytical process due to the ubiquitous nature of fluoropolymers in laboratory applications.

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