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Laboratory-Scale Thermal
Degradation of Fluorocarbon Materials

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Laboratory-Scale Thermal Degradation of Fluorocarbon Materials

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LIST OF ABBREVIATIONS

Abbreviation	Explanation
ATRS	Advanced Thermal Reactor System
d	Diameter
EPA	Environmental Protection Agency
Eqn	Equation
ft	foot, feet
GC/MS	Gas Chromatography / Mass Spectrometry
He	Helium
HPLC	High Performance Liquid Chromatography
i.d.	Internal Diameter
LOD	Limit of Detection
LOQ	Limit of Quantitation
min	minute(s)
NIST	National Institute of Standards and Technology
o.d.	Outer Diameter
PFOA	Perfluorooctanoic acid
QA	Quality Assurance
QAPP	Quality Assurance Program Plans
S/N	Signal to Noise
sec	second(s)
SOP	Standard Operating Protocol
TCD	Thermal Conductivity Detector
TGA	Thermogravimetric Analysis
UDRI	University of Dayton Research Institute
VOC	Volatile Organic Carbon
XPS	X-ray Photoelectron Spectroscopy

Executive Summary

This study reports the first known studies to investigate the thermal degradation of a polyester/cellulose fabric substrate ("article") treated with a fluorotelomer-based acrylic polymer under laboratory conditions conservatively representing typical municipal incineration conditions of time, temperature, and excess air level. The studies emulated typical municipal waste incinerator combustion conditions with an average temperature of 1000°C or greater over approximately 2 sec residence time. The results demonstrate that the polyester/cellulose fabric treated with a fluorotelomer-based acrylic polymer is destroyed and no detectable amount of PFOA is formed under typical municipal incineration conditions. Therefore, textiles and paper treated with such a fluorotelomer-based acrylic polymer disposed of in municipal waste and incinerated are expected to be destroyed and not be a significant source of perfluorooctanoic acid (PFOA) in the environment.

Fluorotelomer-based acrylic polymers (Banks, et al., 1994; Kissa, 2001) are applied to the surface of textiles and paper to impart oil and water repellency to them. Textile fabrics are made from natural (i.e. cotton, wool) and synthetic (i.e. poly-ester, -amide, -propylene) fibers and their blends. Paper is comprised mainly of cellulosic fiber, principally wood pulp. Some paper may also contain fibers such as cotton.

The environmental fate of perfluorinated chemicals, such as fluorotelomer-based substances is of growing interest (Hekster, et al., 2003; Schultz, et al., 2003; Dimitrov, et al., 2004; Stock, et al., 2004). Textiles and paper are often incinerated when they are disposed. No information regarding emissions from incineration of textiles or paper treated with fluorotelomer-based products is available. This study reports the first known studies to investigate the thermal degradation of a polyester/cellulose fabric substrate ("article") treated with a fluorotelomer-based acrylic polymer under laboratory conditions conservatively representing typical municipal incineration conditions of time, temperature, and excess air level. The treated article is reasonably expected to be present in municipal waste as discarded textile or paper. Therefore, the principal focus of this work was to determine the environmental fate of the treated article when it is incinerated.

The test substrate was a fabric comprised of a blend of polyester (ethylene glycol, terephthalic acid) and cellulose fibers. Fabrics with and without a fluorotelomer-based acrylic polymer treatment were tested. The substrate was chosen to be representative of both synthetic and natural fibers that are used in textiles and cellulosic fibers (cotton, wood pulp) used in paper. Fluorotelomer-based acrylic polymers are most commonly used for treating textiles and paper. The fluorotelomer based polymer used was a proprietary DuPont formulation whose composition has been generally described. (US 4742140 and US 5344903)

The test protocols used were similar to those developed for recent testing of fluorinated materials (Yamada and Taylor, 2003; Graham, 2002). Thermogravimetric analysis was used to define the gasification conditions. Thermal experiments were then conducted at non-flame reactor temperatures from 600 to 1000°C for a mean, gas-phase residence time of 2.0 sec. 85% excess air was used for all experiments. The studies emulated typical municipal waste incinerator combustion conditions with an average temperature of 1000°C or greater over approximately 2 sec residence time (Giraud, 2004).

Combustion tests for the treated article, the untreated article, and the fluorotelomer-based acrylic polymer were completed. The following objectives were addressed: 1) determination of the temperature for 99.9% conversion, 2) determination of major products of incomplete combustion at 1000°C for the treated and untreated article, 3) determination of carbon mass balances at 1000°C for the treated and untreated article, 4) determination of the concentration of PFOA in the effluent from all tests, and 5)

determination of the concentration of fluoride ion in the 1000°C tests for the treated and untreated articles.

The temperature for 99.9% destruction of the treated and untreated articles was 725°C. This temperature regime (700-750°C) for 99.9% conversion is consistent with the results of prior tests of hydrocarbon-based materials using UDRI thermal instrumentation systems (Dellinger, et al. 1984; Dellinger, 1989; Taylor, et al. 1990). The temperature for 99.9% destruction ($T_{99.9}$) of the fluorotelomer-based acrylic polymer was 1000°C. The $T_{99.9}$ value for the fluorotelomer-based acrylic polymer was slightly higher than that measured for other fluorinated materials using the same experimental apparatus (Graham, 2002). The difference may be related to the levels of excess air present in the respective combustion tests. Combustion tests with the fluorotelomer-based acrylic polymer used 85% excess air, while previous tests with other fluorinated materials employed considerably higher excess air levels.

Excellent carbon mass balances were obtained from the combustion tests of the untreated and treated articles (101.9 and 103.6%, respectively) at 1000°C. The only product of incomplete combustion that was observed under these conditions was carbon monoxide. Fluorinated organic byproducts were not observed via GC/MS in the combustion tests of the treated and untreated articles. In-line GC/MS was employed to determine the presence of heavier, less volatile fluorinated byproducts. No peaks were detected. Additionally, off-line GC/MS was employed to determine the presence of volatile fluorinated byproducts in the gas exhaust from the 1000°C tests of the treated and untreated articles. No peaks were detected.

Combustion tests of the fluorotelomer-based acrylic polymer were conducted to facilitate interpretation of the treated article combustion results. At 1000°C, 99.9% destruction of the polymer was observed. Based upon this result, the fluorotelomer-based acrylic polymer would be destroyed under typical municipal incinerator conditions. Analysis of the reactor effluent from additional combustion tests of the fluorotelomer-based acrylic polymer indicated the formation of a variety of compounds at temperatures below 1000°C. Many of these compounds could not be identified using either the NIST mass spectral library or manual mass spectral interpretation. As a result, a limited number of combustion experiments were conducted on the Telomer B Alcohol raw material to try to determine the origin of these unidentifiable peaks. The experiments confirmed that selected ions were the same for the polymer and alcohol indicating their origin was indeed from the telomer functionality. Potential volatile combustion byproducts from the combustion of the fluorotelomer-based acrylic polymer were not studied.

Of additional interest was to determine whether PFOA was formed as a result of combustion of the treated article to determine if incineration of treated articles may be a source of PFOA in the environment. Analysis for PFOA in combustion tests of the treated and untreated article at 1000°C using both HPLC/MS/MS and in-line GC/MS were conducted. No detectable level of PFOA was determined. It can therefore be concluded that under typical municipal waste incineration conditions no significant quantity of PFOA would be formed from the incineration of a textile or paper substrate treated with a fluorotelomer-based acrylic polymer.

In addition, transport efficiency tests for PFOA using aqueous sampling (followed by HPLC/MS/MS) and gas-phase sampling (followed by in-line GC/MS analysis) were conducted. Aqueous sampling with HPLC/MS/MS analysis produced transport efficiencies of less than 20% using ATRS reactor and transfer line temperatures of 170°C. Alternatively, in-line GC/MS tests using ATRS reactor and transfer line temperatures of 235°C produced transport efficiencies of greater than 70% (determined by dividing the ATRS PFOA response by the response obtained by direct injection of PFOA into the gas chromatograph). A plausible PFOA loss mechanism during the aqueous sampling transport tests may have involved absorption onto the unheated silicone transfer line tubing between the ATRS vent and the bubblers (see

Fig. 2.15). The basis for this hypothesis was the strong interaction observed between PFOA and the DB-5 capillary column support (phenyl-methyl siloxane) during the in-line GC/MS analysis and the evidence for PFOA condensation in the absorption and transport tests. Cryogenic temperatures were not required to trap PFOA. PFOA was effectively trapped using this column at a temperature of 40°C, thus indicating a strong interaction between the capillary column support and the analyte of interest.

Based upon the combustion product analyses, it was clear that carbon-fluorine bonds were severed at 1000°C. This would result in the formation of fluorine atoms [F]. Fluorine atoms are highly reactive and would be expected to form hydrogen fluoride [HF] by reaction with hydrogen available in the combustion matrix. Analysis for fluoride ion (indicative of HF formation) in combustion tests of the treated and untreated article at 1000°C by trapping the gaseous effluent in aqueous bubblers followed by sampling and ion chromatography indicated fluoride [F^-] below analytical detection limits. Subsequent examination of different sections of the experimental apparatus provided clues as to what happened to the fluoride generated from combustion. XPS analysis of the pyroprobe cartridges used to contain the test sample did not indicate the presence of fluorine on the surface. Removal and visible examination of the high-temperature reactor did, however, indicate significant etching of the reactor surface, most notably downstream of the midpoint of the reactor. This is very likely due to the reaction of hydrogen fluoride (HF) with the silica groups (SiO_2, SiOH) of the reactor surface. Strong evidence confirming this interpretation was obtained from in-line GC/MS total ion chromatograms from the combustion of the fluorotelomer-based acrylic polymer at temperatures between 600 and 1000°C. Silicon tetrafluoride (SiF_4) was observed as a byproduct in these tests. The signal response for SiF_4 showed a near-linear increase with increasing temperature, consistent with increasing yields of HF at higher temperature arising from carbon-fluorine bond breaking. SiF_4 has been observed in previous combustion tests of highly fluorinated materials using high-temperature fused silica reactors (Yamada and Taylor, 2003, Graham, 2002).

To summarize, these results demonstrate that the polyester/cellulose fabric treated with a fluorotelomer-based acrylic polymer is destroyed and no detectable amount of PFOA is formed under typical municipal incineration conditions. Therefore, textiles and paper treated with such a fluorotelomer-based acrylic polymer disposed of in municipal waste and incinerated are expected to be destroyed and not be a significant source of PFOA in the environment.

1. Introduction

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The test substrate was a fabric comprised of a blend of polyester (ethylene glycol, terephthalic acid) and cellulose fibers. Fabrics with and without a fluorotelomer-based acrylic polymer treatment were tested. The substrate was chosen to be representative of both synthetic and natural fibers that are used in textiles and cellulosic fibers (cotton, wood pulp) used in paper. Fluorotelomer-based acrylic polymers are most commonly used for treating textiles and paper. The fluorotelomer based polymer used was a proprietary DuPont formulation whose composition has been generally described. (US 4742140 and US 5344903)

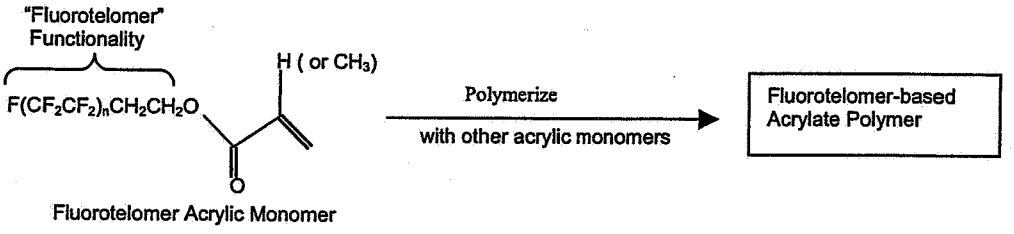


Figure 1.1 Fluorotelomer-based Polymer Description.

2. Experimental Protocol

2.1 Introduction/Objectives

The incineration study was conducted for three samples provided by DuPont: a fluorinated acrylic polymer, untreated articles, and articles treated with the polymer. One major goal of the work was to determine the thermal stability profile of each sample from the sample gasification temperature to a temperature of 99.9% conversion at 50°C increments. Quantitative analysis was also performed for the combustion byproducts CO, CO_2, CF_3H, C_4F_8, and C_8F_{18} at a specified level of conversion. Fluoride and chloride ion were also sampled in aqueous solution and determined. Perfluorooctanoic acid (PFOA) was also sampled using two independent methods and determined. The advanced thermal reactor system (ATRS) with various sampling and analytical techniques was used for the study. The ATRS has been widely used for incineration studies and has been described elsewhere (see Appendix G). The detailed experimental setup, test procedures, analytical methods, and a quality assurance (QA) statement will be discussed in this section.

2.2 Overall Experimental Approach

Sample gasification behavior was investigated using thermogravimetric analysis (TGA) and results are shown in Section 2.4. TGA results were used to determine the sample gasification temperature. The sample materials were fed to the ATRS to incinerate them and analyze their combustion byproducts. An in-line gas chromatography/mass spectrometry (GC/MS) system was used to generate the thermal decomposition profile of each sample and identify major combustion byproducts. Quantitative CO, CO_2, and volatile organic carbon (VOC) determination were performed in separate experiments by collecting effluent from the exhaust line and using off-line GC/thermal conductivity detector (TCD) and GC/MS systems. PFOA, fluoride, and chloride samples were collected in aqueous solution and determined by HPLC/MS/MS and ion chromatagraphy using Exygen, Inc., an analytical laboratory selected by DuPont.

2.3 Samples

2.3.1 Atomic Composition

Tables 2.1 and 2.2 show the weight and atomic compositions of the samples as provided by DuPont.

Table 2.1 Weight Composition (%) of DuPont Samples.

Sample	C	H	F	O	Cl	N
Untreated article	49.1	5.1		45.8		
Treated article	49.7	4.9	0.2	45.2		
Fluorinated acrylic polymer	40.5	4.0	35.5	6.5	13.1	0.3

Table 2.2 Atomic Composition of DuPont Samples.

Sample	C	H	F	O	Cl	N
Untreated article	0.340	0.422		0.238		
Treated article	0.350	0.410	0.001*	0.239		
Fluorinated acrylic polymer	0.334	0.401	0.185	0.040	0.037	0.002*

* Number is neglected for the stoichiometric reaction shown below.

The untreated and treated articles were prepared using a one-hole punch with a diameter of 6 mm ($d \approx 6$ mm) purchased specifically for this project. The fluorinated acrylic polymer was prepared using our

hand-made metal template which gives "hockey-puck" shaped polymer samples (d ≈ 1.6 mm). Relatively uniform dimensions and mass were obtained using these approaches for each sample.

Based on the atomic composition, the stoichiometric oxidation reaction can be written as follows.

* Untreated article

$$C_{0.34}H_{0.42}O_{0.24} + 0.39O_2 \rightarrow 0.34CO_2 + 0.21H_2O \quad \text{---------- (Equation 1)}$$

* Treated article

$$C_{0.35}H_{0.41}O_{0.24} + 0.39O_2 \rightarrow 0.35CO_2 + 0.21H_2O \quad \text{---------- (Equation 2)}$$

* Fluorinated acrylic polymer

$$C_{0.33}H_{0.40}O_{0.04}F_{0.19}Cl_{0.04} + 0.35O_2 \rightarrow 0.33CO_2 + 0.19HF + 0.04HCl + 0.085H_2O \quad \text{--------- (Equation 3)}$$

The amount of oxygen necessary for complete oxidation was used for the gasification time calculation, which is explained in Section 2.4.2.

2.3.2 Thermogravimetric Analysis (TGA) Results

A TGA study was conducted prior to development of the test protocol in order to establish the temperature for complete gasification of each test material. TGA was performed in flowing air using a CSI Model 1050 TGA (Stone-Premco Analytical Instruments) programmed at a heating rate of 25°C/min from room temperature to the point where there is no further weight loss. Approximately 4 mg of sample was gasified with air and the weight % remaining was recorded as function of temperature.

Figures 2.1 and 2.2 show TGA results for untreated and treated articles, respectively. Similar gasification behavior was observed for both samples. Gasification started at 380 and 350°C and ended at 600 and 550°C for untreated and treated articles, respectively. Weight remaining after gasification was 7 and 2.5% for untreated and treated articles, respectively. Figure 2.3 shows TGA results for the fluorinated acrylic polymer. The gasification of the polymer started at around 100°C. Continuous weight loss was observed until 600°C, where nearly 100% gasification was observed.

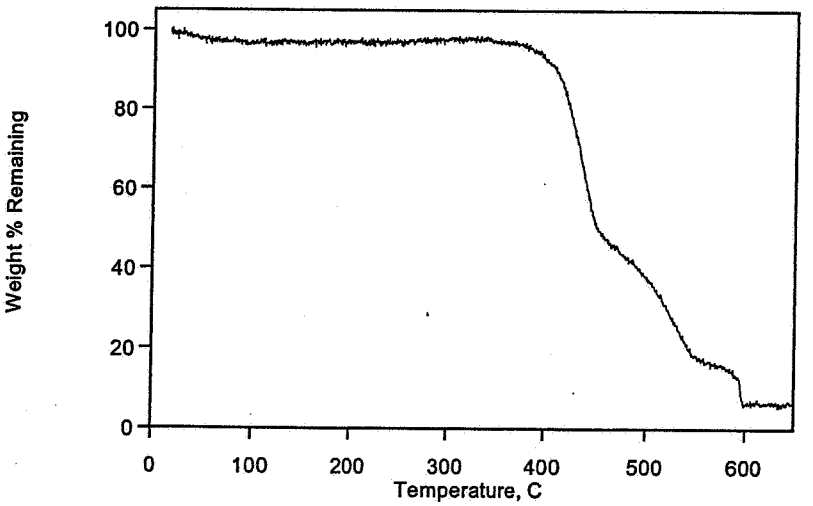


Figure 2.1 TGA Result for Untreated Article.

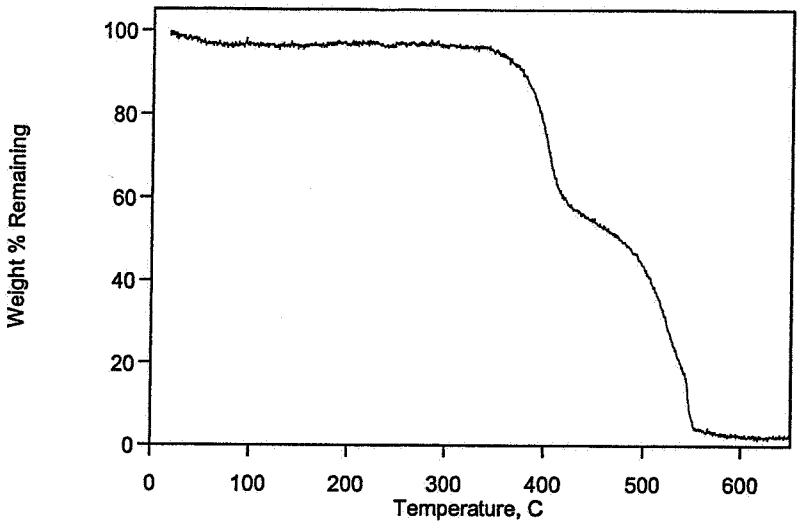


Figure 2.2 TGA Result for Treated Article.

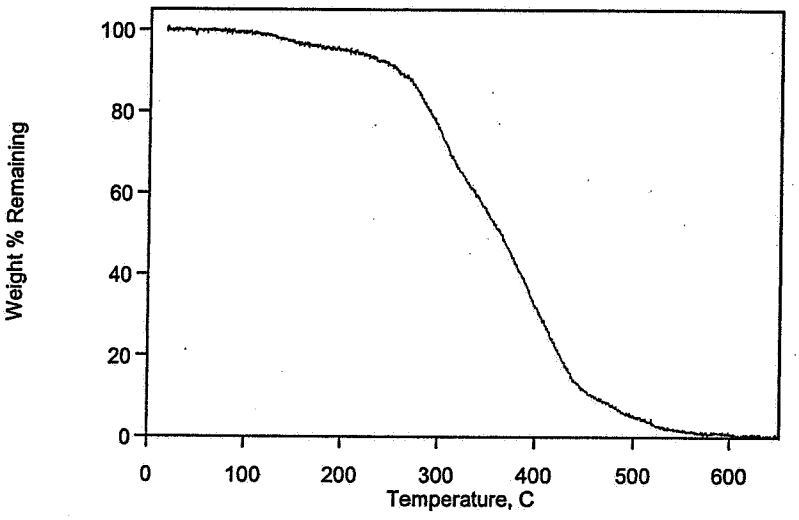


Figure 2.3 TGA Result for Fluorinated Acrylic Polymer.

2.4 In-line GC/MS Analysis and 99.9% Destruction Temperature Determination

2.4.1 Experimental Setup and Procedure for In-line GC/MS Analysis of Combustion Byproducts

Figure 2.4 shows the ATRS, which consists of a sample inlet, reactor, cold trap, and in-line GC/MS system. The sample was placed into a sample cartridge (2 × 2.5 mm (i.d.×o.d.), 12.5 mm length quartz capillary tube, CDS Analytical Inc., Oxford, PA) and the cartridge was inserted into a pyroprobe (CDS-2000). The pyroprobe was placed into Inlet 1 and gasified with synthetic air (21% O_2 and 79% N_2, Airgas Inc.) at 85% excess air to conservatively represent municipal waste combustion conditions (Giraud, 2004). All experiments were performed using synthetic air. The reactor dimensions are 4 × 6 mm

(i.d.×o.d.) with an effective length of 15 cm. The gas residence time was 2.0 sec. All transfer lines were maintained at approximately 300°C for all experiments. Figure 2.5 shows thermocouple locations in the reactor assembly. The temperature at these locations was monitored and recorded before and after the incineration test.

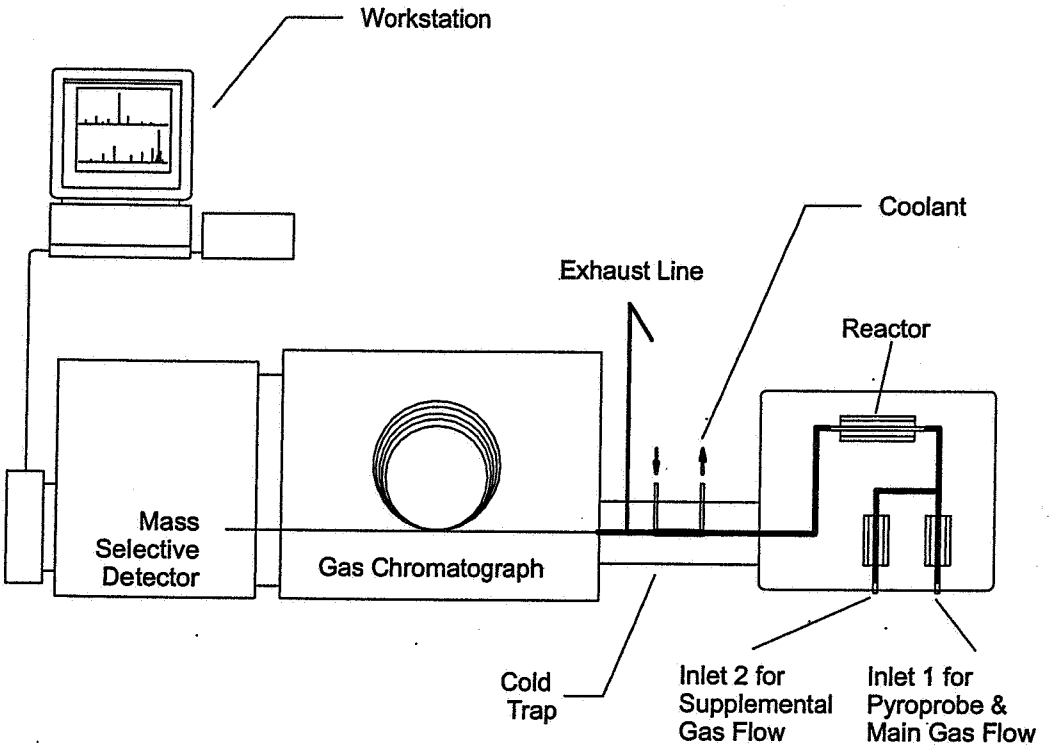


Figure 2.4 General Schematic of the Advanced Thermal Reactor System (ATRS).

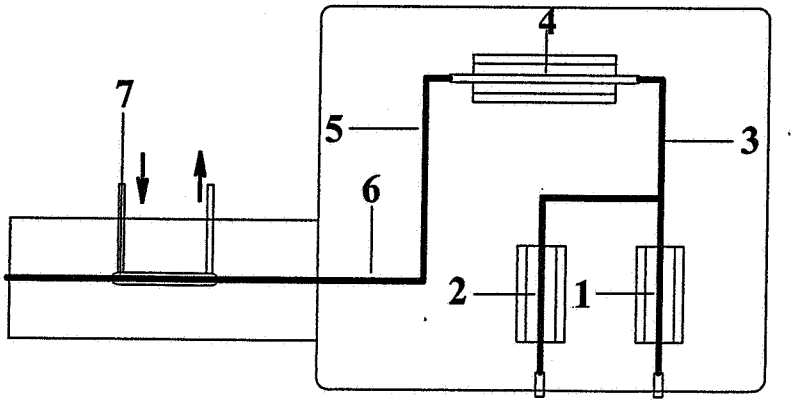


Figure 2.5 Position of Thermocouples in Reactor Assembly.

GC/MS Analysis Method

The gasified sample was incinerated in the reactor, and the combustion byproducts were condensed in the cold trap maintained at -125°C using liquid nitrogen. After combustion was completed, the condensed materials were released when the cold trap was heated to 280°C (with ramping of approximately 45°C/min) and introduced to the GC/MS system for analysis. An HP5890A/5970B series GC-MS with DB-5 GC capillary column (30 m length, 0.25 mm i.d., 0.25 μ film thickness, Agilent Technologies, Inc. Folsom, CA) was used for in-line combustion byproduct analysis. The split ratio was 1 to 24. While the condensed materials were released from the cold trap, the materials were cryogenically trapped at the head of the GC column at -60°C. Following the cryogenic focusing, the oven temperature was held at -60°C for 1 min, then increased to 280°C (with ramping of 20°C/min) and held for 10 min at 280°C. The mass scan range was 12 - 450 m/z to allow analysis of a wide range of compounds including water. The actual sample combustion procedure was performed in sequence as follows:

1. Set air flow rate to obtain residence time of 2 sec at the reactor. Two thirds of the flow is introduced to Inlet 1 where the pyroprobe is inserted and one third of the flow is introduced to Inlet 2.
2. Record ATRS inlet flow rates.
3. Set cold trap temperature to -125°C using liquid nitrogen.
4. Record temperature at the 7 points shown in Figure 2.4.
5. Insert pyroprobe into Inlet 1.
6. Stabilize the system for 2 min.
7. Start pyroprobe temperature programming.
8. Remove pyroprobe.
9. Sweep entire system with helium (He) for 3 min.
10. Record ATRS inlet flow rates.
11. Record temperature at 7 points shown in Figure 2.5.
12. Set GC column temperature to -60°C using liquid nitrogen.
13. Start GC/MS analysis.
14. Heat cold trap to 280°C to release condensed materials from the trap and transfer them to GC/MS.

2.4.2 ATRS Experimental Conditions

Flow Rate

The reactor volume of 1.88 cm^3 (0.2 cm i.d., 15 cm effective length) and residence time of 2.0 sec gives a fixed flow rate of 0.94 mL/sec at 25°C. This flow rate was corrected with the reactor temperature as shown below:

$$0.94 \text{ mL/sec} \times 298 / (T + 273) \qquad \text{---------- (Equation 4)}$$

(T: Reactor Temperature in °C)

Gasification Temperature and Duration

Table 2.3 shows initial and final temperatures of the pyroprobe. Based on the TGA results, the initial and final temperature of the untreated and treated articles were set at 350 and 650°C, respectively. Although the TGA results indicated that the final gasification temperature for the untreated article is 50°C higher than the treated article, the pyroprobe final gasification temperatures for both materials were set at the same level for consistency and to facilitate comparison of results. The temperatures for both materials

were identical for consistency. The initial and final temperatures for the fluorinated acrylic polymer were set at 250 and 650°C, respectively. The temperature ramping rates between the initial and final temperatures were varied to adjust gasification time and obtain appropriate stoichiometric conditions as described in more detail below. The temperature of Inlet 1 was set at 300°C for the untreated and treated articles and 250°C for the fluorinated acrylic polymer. The inlet temperature for the fluorinated acrylic polymer was reduced to prevent significant weight loss during system stabilization after sample insertion and before gasification.

Table 2.3 Pyroprobe Gasification Temperature (°C).

Sample	Initial	Final	Inlet 1 Temperature
Untreated article	350	650	300
Treated article	350	650	300
Fluorinated acrylic polymer	250	650	250

Because the reactor volume and residence time are fixed parameters, the flow rate cannot be changed to set the excess air level. Therefore, the gasification time and amount of sample are the two adjustable parameters to obtain 85% excess air. Since it is not practical with existing equipment to prepare the desired amount of samples with 10 μg precision, the gasification time is the only parameter that can be varied to obtain the desired ratio. The calculation below shows how the gasification time for the fluorinated acrylic polymer was determined.

Suppose the weight of the fluorinated acrylic polymer used for combustion at 600°C is 2.25 mg. The molecular weight of the hypothetical polymer shown in Eqn 3 is 9.88. The molar amount of polymer in this sample is $2.25/1000(g)/9.88(g/mol) = 2.28 \times 10^{-4}$ moles.

From the stoichiometric reaction for the polymer (Eqn 3 in Section 2.3.1), the oxygen required can be calculated as:

$2.28 \times 10^{-4} mol \times 0.35$

The volume of air (21% oxygen and 79% nitrogen) in units of mL with 85% excess air ($85\% \times 0.21 = 17.85\%$ excess oxygen) at 1 atm and 298°C can be calculated as:

$[2.28 \times 10^{-4}(mol) \times 0.35 \times 1.1785 \times 0.0821(atm^{-1}/mol\text{-}K) \times 298(K) / 1(atm)] / 0.21 \times 1000(mL/l) =$
$11.0\ mL$

The flow rate at 600°C is

$0.94(mL/sec) \times 298\ (K) / (600 + 273)\ (K) = 0.32\ mL/sec.$

The gasification time can then be calculated as follows:

$11.0\ mL/0.32(mL/sec) = 34.4\ sec$

Since the initial and final gasification temperatures for the polymer are 250 and 650°C, respectively, as discussed above, the pyroprobe temperature was linearly increased from 250 to 650°C with a ramping rate of:

$(650\text{-}250)°C/34.4\ sec \times 60\ sec/min = 698°C/min$

The key assumptions are that gasification starts when the pyroprobe temperature programming for the polymer starts (250°C) and ends at the final temperature (650°C), and sample weight loss is linear with time.

2.4.3 GC/MS Calibration

Calibration curves were created for the compounds of interest based on prior work: CF_3H (98+%, Lot #: 22912MI, Aldrich, Milwaukee, WI), C_4F_8 (98% minimum, Lot #: 8B-110, SynQuest Labs., Inc., Alachua, FL), and C_8F_{18} (98%, Batch #: 17024MA, Aldrich, Milwaukee, WI). The results are shown in Figures 2.6 through 2.8. The detection limit was determined based on EPA's detection limit criteria for identifying an unknown (EPA Method 8260B, pages 23 – 24). In this analysis, we chose the most abundant ion (target ion) and major ions whose intensities were greater than ca. 20% of the target ion. The detection limit was the lowest concentration that had the target ions and all of major ions whose relative intensity also agreed with the reference spectra within ca. ± 20%. Calibration and detection limit determination were consistent with prior thermal decomposition studies conducted in this laboratory (Taylor, et al., 1995, 1996,; Tirey, et al., 1990; Wehrmeier, et al., 1998). The following procedure was used to construct each calibration curve.

> A known amount of each standard was introduced into Inlet 1 in the reactor assembly. All transfer lines and the reactor was heated at 300°C. Standards were condensed at the cold trap at -125°C, and then transferred to the GC/MS system for analysis. The procedure was exactly the same as in the combustion tests of samples. The major ion from each standard was extracted (69 for CF_3H and C_8F_{18}, and 131 for C_4F_8) and plotted as the function of the injected molar quantity.

Figures 2.6 - 2.8 shows calibration curves for CF_3H, C_4F_8, and C_8F_{18}, respectively. The linear fit equation and detection limit for each standard are summarized in Table 2.4. The detection limit improves with molecular size. This is probably due to an increased MS response factor and better peak shape obtained from the DB-5 GC capillary column (30 m length, 0.25 mm i.d., Agilent Technologies, Inc. Folsom, CA) with increased molecular size.

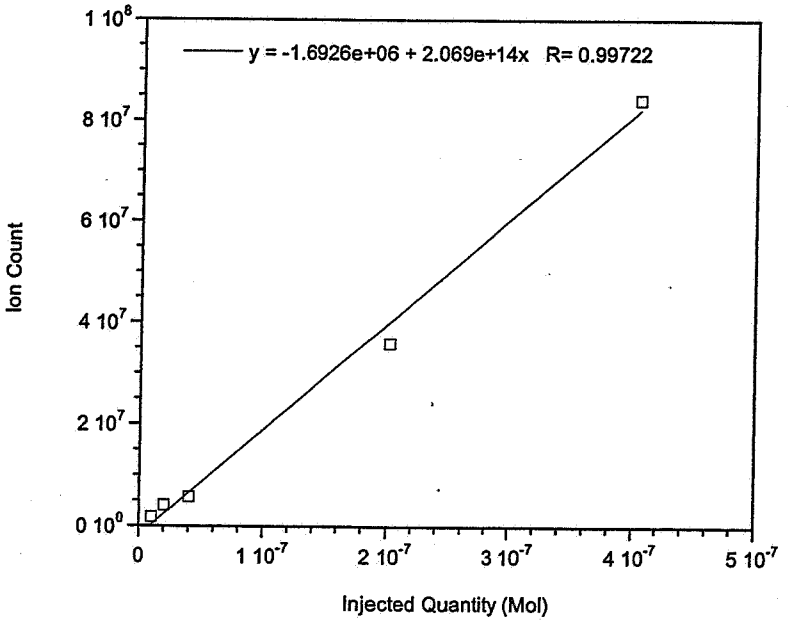


Figure 2.6 CF_3H Calibration Curve.

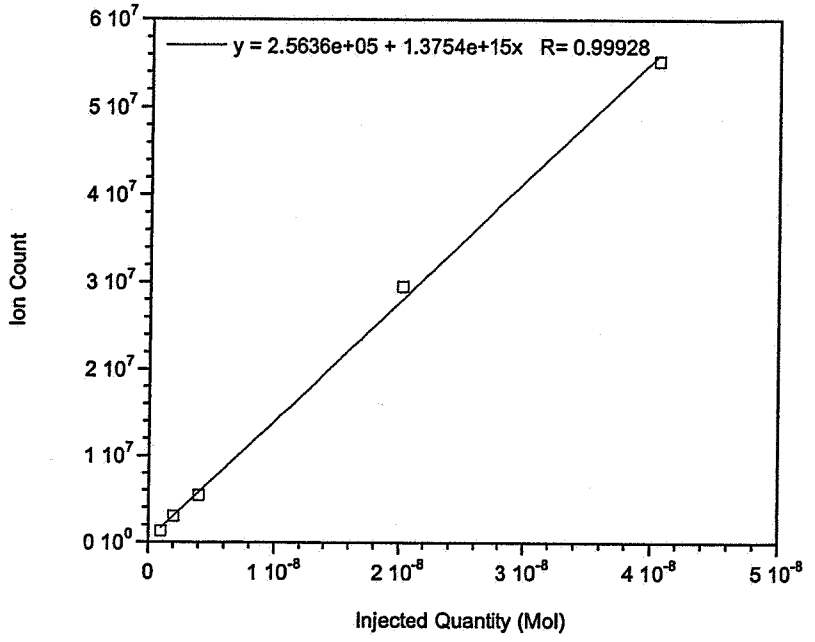


Figure 2.7 C_4F_8 Calibration Curve.

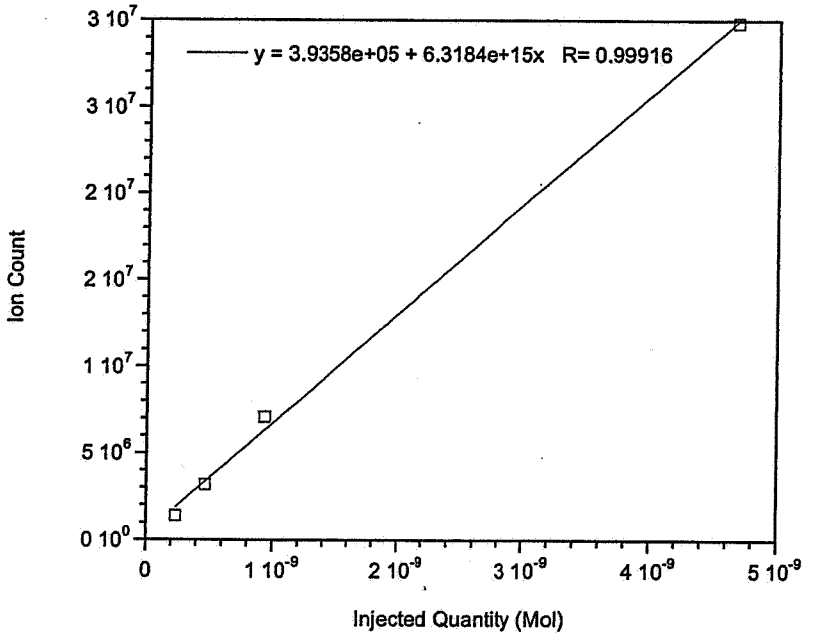


Figure 2.8 C_8F_{18} Calibration Curve.

Table 2.4 Linear Fit Equations for Standard Calibration Curves and Detection Limits.

Sample Name	Linear Fit (x: mol, y: peak area)	R	Detection Limit (mol)
CF_3H	$x = (y + 1.69E6)/2.07E14$	0.997	1.01E-8
C_4F_8	$x = (y - 2.56E5)/1.38E15$	0.999	1.01E-9
C_8F_{18}	$x = (y - 3.94E5)/6.32E15$	0.999	2.34E-10

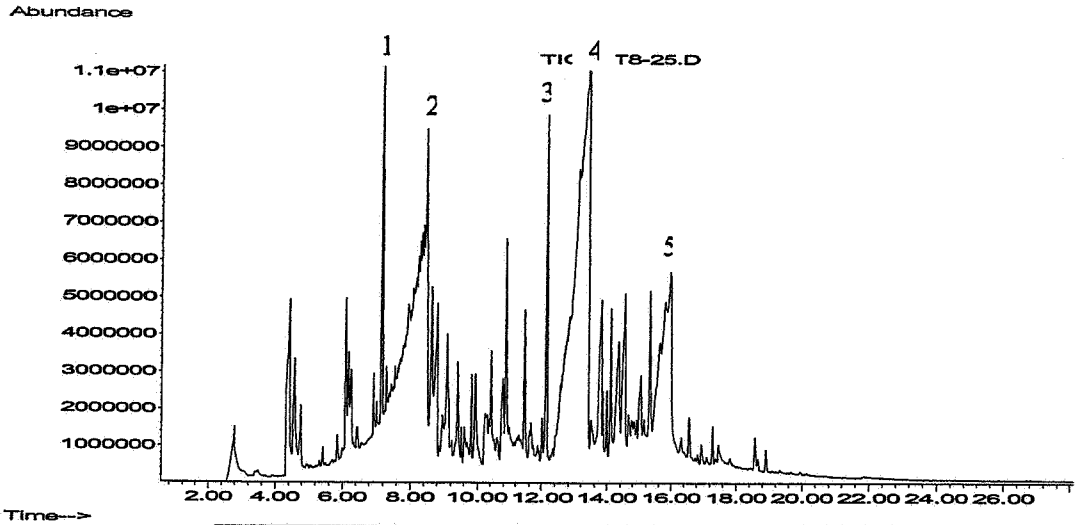
2.4.4 GC/MS Determination of Major Ions for Construction of Thermal Decomposition Profile

Preliminary tests were conducted to identify the chemical species associated with the major peaks and determine major ions that could be used for construction of the thermal decomposition profile. The ions used were 122 (benzoic acid) and 149 (terephthalic acid derivative) for the untreated and treated article, and 69 (CF_3) and 77 ($C_3F_2H_3$) for the fluorinated acrylic polymer.

Treated and Untreated Articles

Thermal testing was initiated at 600°C. The total ion chromatogram obtained at this temperature was presumably from simple gasification products with minimal oxidation. Preliminary tests indicated that benzoic acid was the largest peak for untreated and treated articles at 600°C. Figure 2.9 shows a total ion chromatogram of the untreated article at 600°C, and Figure 2.10 shows the mass spectrum at 13.4 min, where the largest signal is located. Comparison of the sample and library spectra indicates benzoic acid with 91% match quality. The first large peak at 8 min is due to the formation of water. The peak at 16 min has strong ion of 149 and is most likely a terephthalic acid derivative.

Figure 2.11 shows a total ion chromatogram of the treated article combustion at 600°C and Figure 2.12 shows mass spectra at 13.5 min, where the largest peak is located. Similar results were obtained for both treated and untreated articles. Benzoic acid and terephthalic acid are expected thermal decomposition products of polyester (Ohtani, et al., Radlein, et al., 1991). The areas of all peaks were integrated within a mass range between 35 and 450 m/z to eliminate the peak associated with water from the analysis, and the ratio of these two peaks were calculated. The results showed that the benzoic acid peak consists of 33 and 36% of total peak area for untreated and treated articles, respectively, and the terphthalic acid derivative peak consists of 13% of the total peak area for both samples. The total integrated peak area of these extracted ions (122 and 149) was used for constructing the thermal decomposition profiles for the treated and untreated articles. The results are summarized in Section 3.1.1 and 3.1.2.



ID #	Compound Name	Quality (%)[a]
1	Benzene	96
2	Toluene[b]	94
3	1-Phenyl-1,2-propanedione	91
4	Benzoic acid	91
5	Terephthalic acid derivative[c]	78

[a] Match quality from NIST129K standard spectra library, obtained by data analysis software (G1701BA Version B03.00, Agilent Technologies). [b] Toluene is located on top of the large water peak. [c] This compound could not specifically be identified, but is most likely a terephthalic acid derivative based on manual mass spectral analysis.

Figure 2.9 Total Ion Chromatogram and Peak Identification for Untreated Article at 600°C.

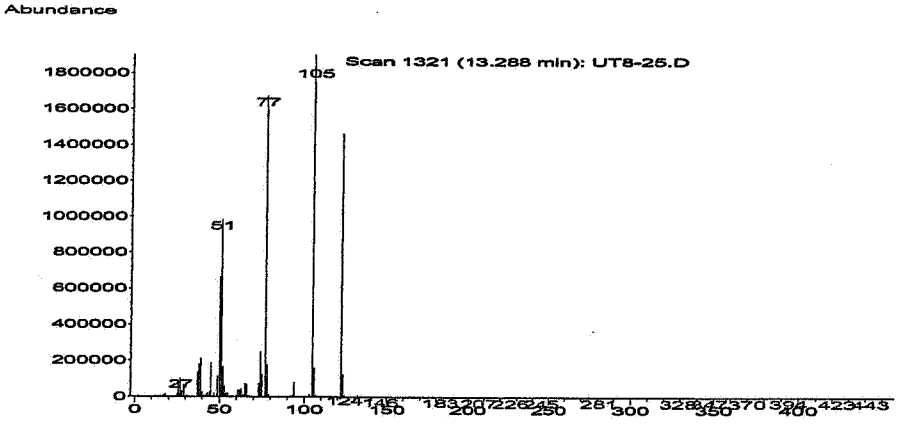
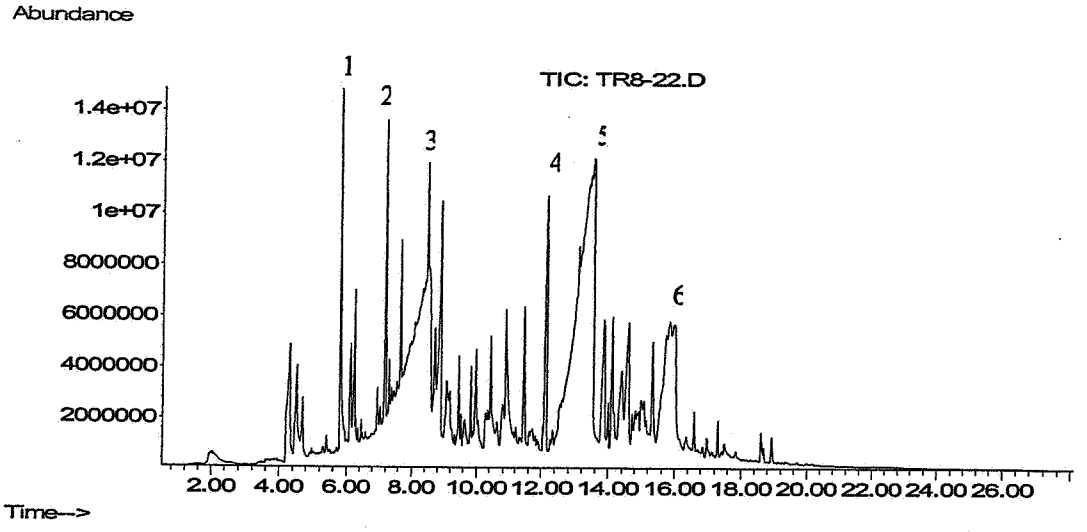


Figure 2.10 Mass Spectra at 13.4 min for Untreated Article at 600°C.



ID #	Compound Name	Quality (%)[a]
1	Water[b]	1
2	Benzene	96
3	Toluene[c]	91
4	1-Phenyl-1,2-propanedione	91
5	Benzoic acid	81
6	Terephthalic acid derivative[d]	64

[a] Match quality from NIST129K standard spectra library, obtained by data analysis software (G1701BA Version B03.00, Agilent Technologies). [b] The low matching quality is due to number of small background ions in the spectrum. The major ions clearly indicate water. [c] Toluene is located on top of the large water peak. [d] The compound could not specifically be identified, but is most likely a terephthalic acid derivative based on manual mass spectral analysis.

Figure 2.11 Total Ion Chromatogram and Peak Identification for Treated Article at 600°C.

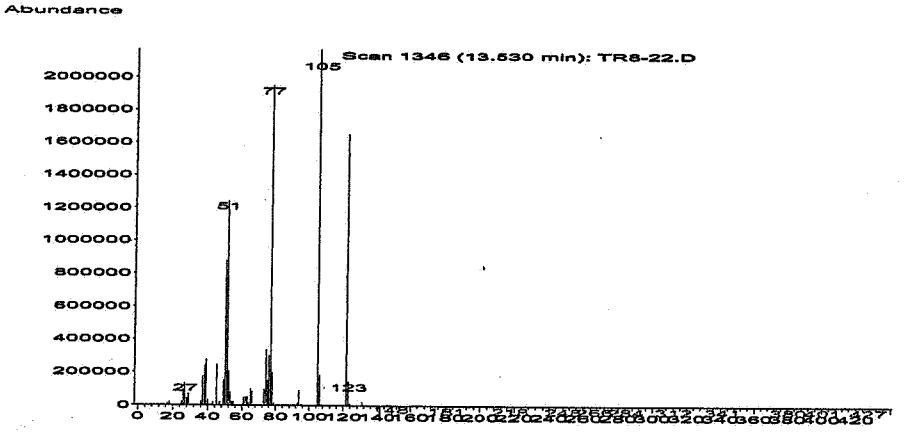
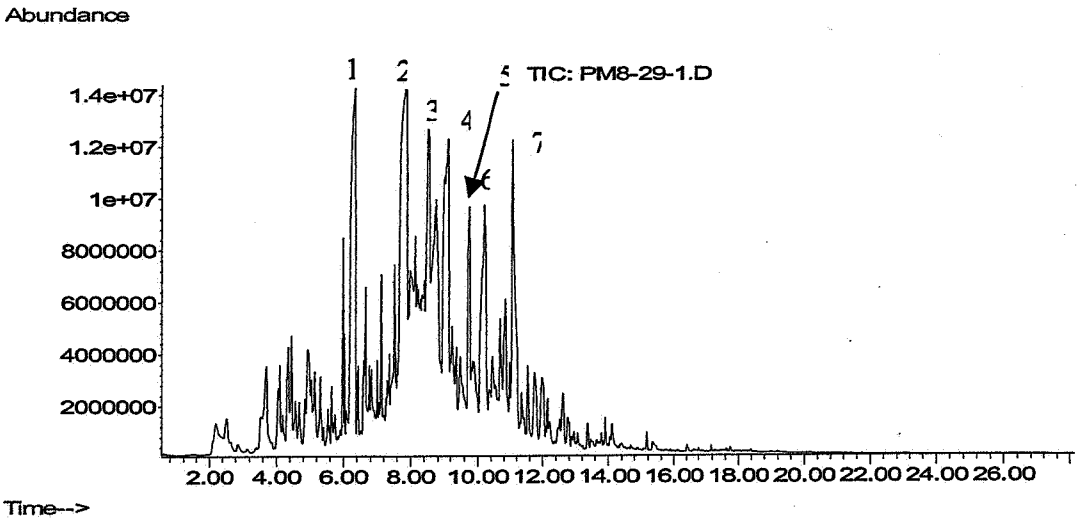


Figure 2.12 Mass Spectra at 13.5 min for Treated Article at 600°C.

Fluorinated Acrylic Polymer

Figure 2.13 shows the total ion chromatogram of the fluorinated acrylic polymer combustion at 600°C. The baseline elevation at 8 min is due to formation of water. The baseline also indicates the presence of ion 85 which is indicative of the formation of silicon tetrafluoride (SiF_4). This product is associated with oxidation of the polymer and subsequent reaction of hydrogen fluoride with test system materials. The extent of formation of SiF_4 was monitored in each run to determine its potential impact on the fluorine recoveries.

Several peaks were identified as fluorinated and chlorinated hydrocarbons. Figure 2.14 shows extracted ions 69 and 77, which are the major ions for the major peaks identified. The structures of these ions were suggested by the NIST library and are plausible combustion byproducts. The total peak area of these extracted ions (69 and 77) was used as reference ions for constructing the thermal decomposition profile for the polymer. The combustion byproducts of interest were quantified at each reactor temperature. The results are summarized in Section 3.1.3.



ID #	Compound Name	Quality (%)[a]
1	Not identifiable[b]	
2	3,3,4,4,-tetrafluoro-1,5-hexadiene[c]	45
3	Not identifiable[a]	
4	Not identifiable[a]	
5	1,1,3-trichloro-2-Propanone[c]	47
6	Perfluoro-n-pentanoic acid	90
7	Not identifiable[a]	

[a] Match quality from NIST129K standard spectra library, obtained by data analysis software (G1701BA Version B03.00, Agilent Technologies). [b] Not identifiable due to low match quality. [c] The compound showed is the best match to the library, but not reliable because of the low match quality.

Figure 2.13 Total Ion Chromatogram and Peak Identification for Fluorinated Acrylic polymer at 600°C.

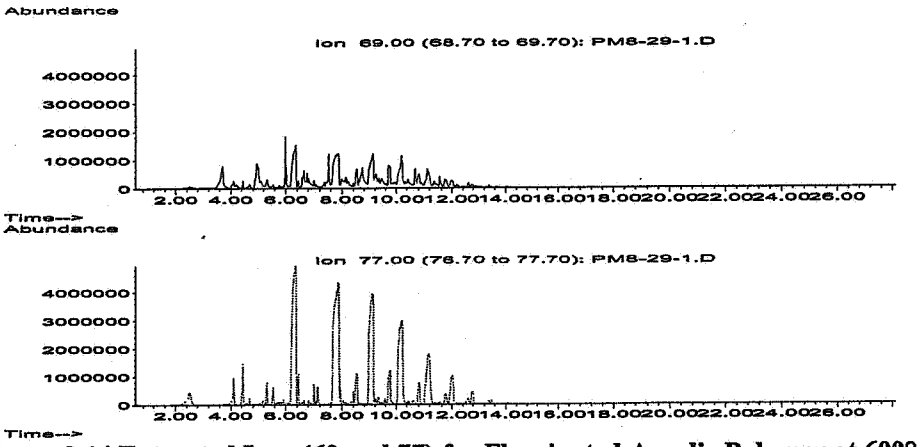


Figure 2.14 Extracted Ions (69 and 77) for Fluorinated Acrylic Polymer at 600°C.

2.5 Treated and Untreated Articles: PFOA, Fluoride, and Chloride Determination at 1000°C

The reactor effluent from the combustion of the treated and untreated articles was sampled and PFOA, fluoride, and chloride were determined. The samples were gasified and incinerated in a similar manner to the procedure described in section 2.4.1. The entire system, including cold trap, was heated to 300°C. As shown in Figure 2.15, the effluent was taken from the exhaust vent and passed through an aqueous solution bubbler system to collect the analyte of interest. The bubbler system consisted of two bubblers (120 mL amber glass jar, I-CHEM, New Castle, DE) with 1 × 3 mm i.d. × o.d., 4 in length quartz stem filled with 60 mL HPLC grade water (HPLC Grade Ultrapure Water, Stock #22934, Lot #L10N39, Alfa Aeser, Ward Hill, MA) as shown in Figure 2.15. The silicone tubing (0.063 in i.d., 0.125 in o.d., 12 in length, Cole Parmer Instrument Co., Vernon Hills, IL) was used as a transport line between the exhaust vent and first bubbler. The same tubing, approximately 2 in in length, was used to connect the two bubblers. An additional thermocouple was placed downstream of the bubblers as shown in Figure 2.15 and the temperature monitored and recorded. Following each experiment, the silicone tube that connects the exhaust line and the first bubbler was rinsed with 5 mL HPLC grade water (Alfa Aesar) and the extracts added to the first bubbler. The sample was sealed with an aluminum foil sealer, labeled, and sent to Exygen with chain of custody form for the analyses. The actual sampling was performed as follows:

1. Set airflow rate to obtain residence time of 2 sec at the reactor. Two thirds of the flow was introduced to Inlet 1 where the pyroprobe is inserted and one third of the flow was introduced to Inlet 2.
2. Record ATRS inlet flow rates.
3. Set cold trap temperature to 300°C (no condensation step).
4. Record temperatures at the 8 points shown in Figure 2.4 and 2.15.
5. Connect bubblers to exhaust line.
6. Insert pyroprobe into Inlet 1.
7. Stabilize the system for 1 min.
8. Start pyroprobe temperature programming.
9. Sweep entire system with helium for 3 min.
10. Record temperature downstream of second bubbler.
11. Disconnect bubblers
12. Record ATRS inlet flow rates.
13. Record temperatures at the 8 points shown in Figure 2.4 and 2.15.

The results are summarized in Section 3.2.

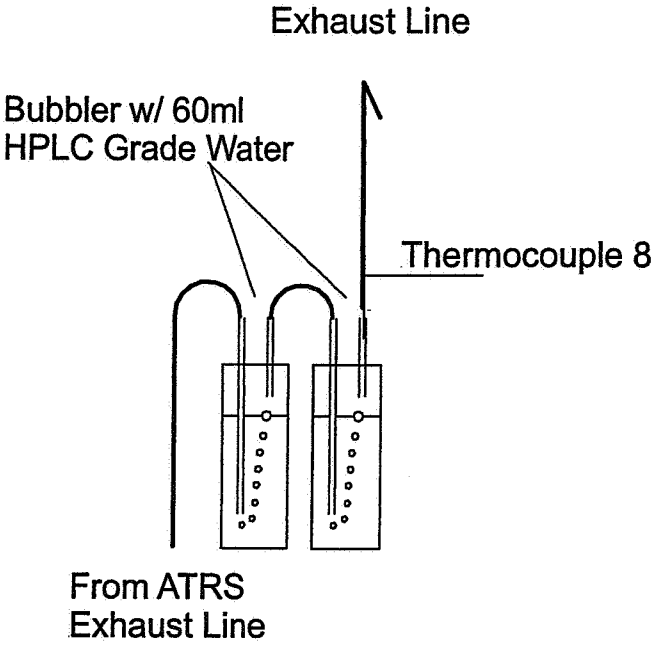


Figure 2.15 Off-Line Aqueous Sampling for Fluoride and PFOA.

2.6 Treated and Untreated Articles: Off-line GC/MS Analysis of Volatile Organic Compound (VOC) Analysis at 1000°C

The reactor effluent from the combustion of the treated and untreated articles was analyzed for volatile organic compounds at 1000°C using a gas sampling bag and off-line GC/MS analysis. The sample was taken from the exhaust line shown in Figure 2.4 using a 0.5 L Tedlar® bag (SKC Inc., Eighty Four, PA). Silicone tubing (0.063 in i.d., 0.125 in o.d., 30 cm length, Cole Parmer Instrument Co., Vernon Hills, IL) was used for the transfer line. The collected sample was used for both VOC and fixed gas (CO, CO_2) analyses (see Section 2.7). The sample was gasified and incinerated in a manner similar to the in-line GC/MS analysis. The entire system, including cold trap, was heated at 300°C for this analysis. The detailed procedure is shown below. A Supelco Q PLOT column (30 m × 0.53 mm ID, SUPELCO Inc., Bellefonte, PA) was used for analysis and the injection volume was 0.5 mL. The GC oven temperature was held at -60°C for 1 min, then increased to 280°C with ramping of 20°C/min and held 5 min at 280°C. The mass scan range was 12 - 450 m/z to allow analysis of a wide range of compounds including water. The sampling procedure is shown below:

1. Set air flow rate to obtain residence time of 2 sec at the reactor. Two thirds of the flow is introduced to Inlet 1 where the pyroprobe is inserted and one-third of the flow is introduced to Inlet 2.
2. Record inlet flow rate.
3. Set cold trap temperature to 300°C (no condensation step).
4. Record temperatures at 7 points shown in Figure 2.4.
5. Insert pyroprobe into Inlet 1.
6. Stabilize the system for 1 min.
7. Connect Tedlar® bag to exhaust line and open valve.
8. Start pyroprobe temperature programming.

9. Sweep entire line with He for 3 min.
10. Close Tedlar® bag valve and disconnect a bag.
11. Record inlet flow rate.
12. Record temperatures at 7 points shown in Figure 2.4.

The results are summarized in Section 3.6.

2.7 Treated & Untreated Articles: CO and CO_2 Analyses at 1000°C

The samples collected for VOC analysis were also used for CO and CO_2 analyses. The CO and CO_2 were analyzed using a GC/TCD (8610C gas chromatograph, SRI Instruments, Torrance, CA). CO and CO_2 were separated from other compounds using a 6 ft molecular sieve packed column and silica gel column, respectively, which were preinstalled by the manufacturer (SRI Instruments). A standard calibration was conducted prior to the analyses; results are shown in Figures 2.16 and 2.17. Table 2.5 shows the linear fit equation of CO and CO_2 calibration. Carbon mass balance was calculated based on the sample gasified and the amounts of VOC, CO, and CO_2 measured. The results are summarized in Section 3.7

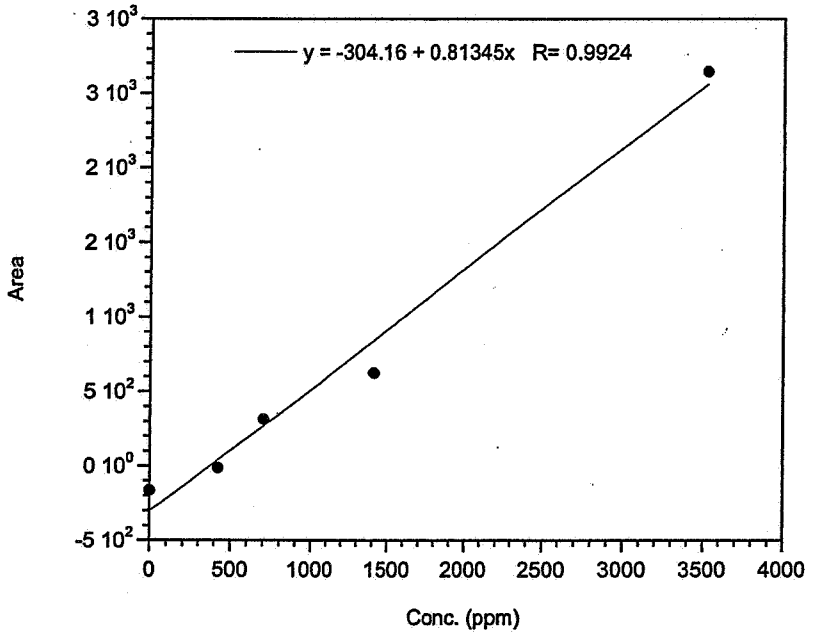


Figure 2.16 CO Calibration Curve.

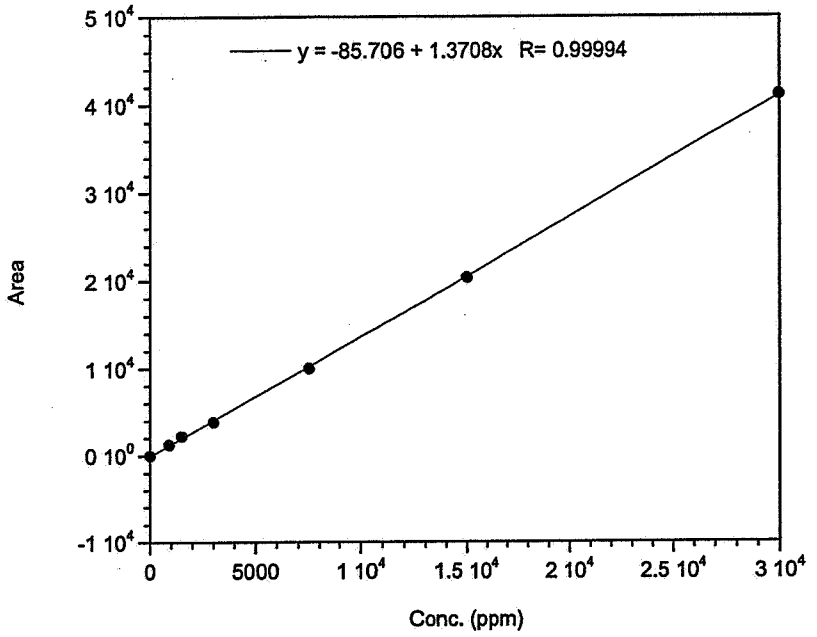


Figure 2.17 CO_2 Calibration Curve.

Table 2.5 Linear Fit Equations for CO and CO_2 Calibration Curves.

Sample Name	Linear Fit (x: mol, y: peak area)	R
CO	$x = (y + 3.04E2)/8.13E\text{-}1$	0.992
CO_2	$x = (y + 8.57E1)/1.37E0$	0.999

2.8 XPS Analysis of Pyroprobe Cartridge

The surface of the sample cartridge used for treated article gasification was analyzed by x-ray photoelectron spectroscopy (XPS) to investigate fluoride deposition on the cartridge surface. The results are summarized in Section 3.4

2.9 Telomer B Alcohol Combustion: GC/MS Analysis

In-line GC/MS analysis was conducted for Telomer B Alcohol combustion at 200 and 600°C to investigate if the 77 ion observed in the combustion tests of the fluorinated acrylic polymer is formed. Ion 77 is the most abundant ion of the fluorinated acrylic polymer combustion byproduct effluent according to the preliminary combustion tests (see Section 2.4.4). The Telomer B Alcohol is a multi-component mixture whose formula and concentration range are shown in Table 2.6. The generic formula is estimated based on the average concentration of each constituent and can be expressed as:

$C_{0.30}F_{0.52}H_{0.15}O_{0.03}$

Due to a scarcity of hydrogen in the test substance, methane was also supplied as a hydrogen source to convert excess fluorine to HF. Methane was supplied at twice the stoichiometric amount to ensure fluorine conversion to HF. A 10 mL gas tight syringe (SGE, Austin, TX) and syringe pump (Kd Scientific, Holliston, MA) was used to supply methane. The stoichiometric oxidation can be expressed as follows:

$C_{0.30}F_{0.52}H_{0.15}O_{0.03} + 0.185CH_4 + 0.5625O_2 \rightarrow 0.485CO_2 + 0.52HF + 0.185H_2O$ ---------- (Equation 5)

The sample inlet and transfer lines were kept at 150°C. Pyroprobe initial and final temperatures were set at 150 and 200°C, respectively, and the final temperature was held for 1 min to ensure complete gasification. Two tests were conducted at reactor temperatures of 200°C and 600°C. The results are summarized in Section 3.5.

Table 2.6 Telomer B Alcohol Characterization.

Name	Formula	Conc. Range (%)	Average Conc. (%)
1,1,2,2-Tetrahydroperfluoro-1-Hexanol	$CH_2OHCH_2(CF_2)_3CF_3$	1 – 2	1.5
1,1,2,2-Tetrahydroperfluoro-1-Octanol	$CH_2OHCH_2(CF_2)_5CF_3$	27 – 34	30.5
1,1,2,2-Tetrahydroperfluoro-1-Decanol	$CH_2OHCH_2(CF_2)_7CF_3$	29 – 34	31.5
1,1,2,2-Tetrahydroperfluoro-1-Dodecanol	$CH_2OHCH_2(CF_2)_9CF_3$	17 -21	19
1,1,2,2-Tetrahydroperfluoro-1-tetradecanol	$CH_2OHCH_2(CF_2)_{11}CF_3$	6 – 9	7.5
1,1,2,2-Tetrahydroperfluoro-1-Hexadecanol	$CH_2OHCH_2(CF_2)_{13}CF_3$	2 – 5	3.5
1,1,2,2-Tetrahydroperfluoro-1-Octadecanol	$CH_2OHCH_2(CF_2)_{15}CF_3$	1 – 2	1.5

2.10 Perfluorooctanoic Acid (PFOA) Absorption Study

An independent system was built to study PFOA absorption. The purpose of the absorption test was to study how much PFOA can be transferred from the gas phase to the aqueous solution. This set of experiments examined the absorption efficiency of PFOA into aqueous solution and sought to examine the propensity in which PFOA may condense in the test system.

2.10.1 PFOA Absorption Study

Figure 2.18 shows a schematic of the PFOA absorption study apparatus. PFOA was weighed and placed into a sample container (2×2.5mm (i.d.×o.d.), 25 mm length quartz capillary tube, CDS Analytical Inc., Oxford, PA), which was also weighed prior to sample loading. The sample container was placed into a heating tube (4×6 mm (i.d.×o.d.), 20 cm length). The aqueous absorption system consisted of two 120 mL glass jars, each containing 60 mL HPLC grade water (HPLC Grade Ultrapure Water, Stock #22934, Lot #L10N39, Alfa Aeser, Ward Hill, MA). Silcosteel® tubing (1/8 in) (RESTEC Co., Bellefonte, PA) was used as a transfer line between the heating tube and bubbler. The heating tube and transfer line was heated from room temperature to 170°C with a temperature ramping rate of approximately 25°C/min and held at 200°C for 5 min. The vaporized PFOA was swept using carrier flow (synthetic air) at 19.2 mL/min flow rate and bubbled through the aqueous solution. The sample container was weighed again after heating. The molar amount of PFOA available for absorption was calculated from the difference in weight before and after heating. This amount was compared to PFOA determined in aqueous solutions to calculate the absorption efficiency.

The heating tube and Silcosteel® (RESTEC Co., Bellefonte, PA) transfer line were rinsed with 60 mL HPLC grade water (Alfa Aeser) and collected into jar 3. This was to facilitate capture of PFOA condensed on heating tube and transfer line walls.

Each aqueous sampling jar was labeled, secured, and sent to Exygen with a chain of custody form for PFOA determination. The results of these studies are summarized in Section 3.8.

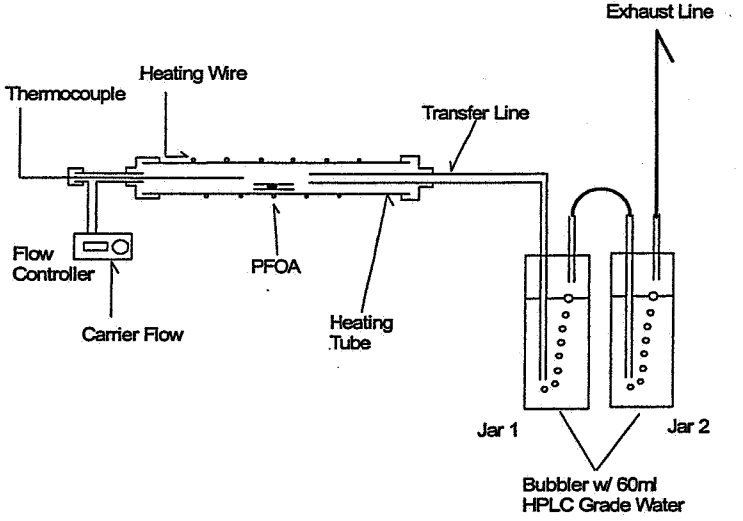


Figure 2.18 Schematic for PFOA Absorption Test.

2.11 PFOA Transport Studies

In order to evaluate the transport of PFOA through the ATRS, two independent experiments were conducted. First, PFOA in the ATRS effluent was sampled in an aqueous solution bubbler system for HPLC/MS/MS analysis. Second, PFOA in the ATRS effluent was sampled and analyzed using in-line GC/MS analysis.

2.11.1 PFOA Transport Study - Aqueous Sampling

Two tests were conducted using the same ATRS setup used for PFOA, fluoride, and chloride sampling and analyses described in Section 2.5. The temperature for the first test was 170°C, and the temperature for the second test was 300°C. All transfer lines, reactor, and cold trap were maintained at the same temperature to prevent sample condensation and decomposition. The injection ports were kept at 170°C for both 170 and 300°C transport tests. The sample was placed into a sample cartridge (2 × 2.5 mm (i.d.×o.d.), 12.5 mm length quartz capillary tube, CDS Analytical Inc., Oxford, PA) and the cartridge inserted into Inlet 1 using the pyroprobe and gasified at 170°C. The pyroprobe temperature was increased from 100°C to 170°C at the rate of 70°C/min and held 170°C for 4 min giving a total of 5 min. The ATRS effluent was passed through two aqueous solution bubblers connected in series to collect PFOA as shown in Figure 2.15. The transfer line (12 in silicone tubing (0.063 in i.d., 0.125 in o.d., Cole Parmer Co., Vernon Hills, IL)), was rinsed with 5 mL HPLC grade water (HPLC Grade Ultrapure Water, Stock #22934, Lot #L10N39, Alfa Aeser, Ward Hill, MA), and added to Jar 1.

After PFOA was collected in the aqueous solutions, a low pressure steam extraction procedure was performed to extract any possible PFOA condensate remaining in the ATRS system. The steam was collected from the ATRS exhaust line and condensed into two glass vials (40 mL Vial, Amber, Wheaton, Millville, NJ) which were connected in series and immersed in an ice bath as shown in Figure 2.19. The following procedure was used for steam extraction.

The entire ATRS system (inlet, reactor, transport line, and cold trap) was heated to 300°C prior to steam extraction. 5 mL of HPLC grade water (Alfa Aeser) was injected into inlet 1 using a syringe pump (Model 101, Kd Scientific Inc., Holliston, MA) and a 5 mL syringe. Steam was generated by injection to inlet 1 heated to 300°C. The syringe pump was used to inject water at a constant rate. The steam was collected as condensate using two 40 mL vials which were placed in the ice bath.

The steam injection flow rate was limited to 200 mL/min at 300°C. Five mL of HPLC grade water (Alfa Aesar) was injected at a rate of 4 mL/hr, generating 174 mL/min steam flow through the system. The extraction procedure was performed five times consecutively. Vial 1 was weighed before and after the steam extraction procedure to measure the amount of water condensed. Vial 2 was not weighed because there was no visible condensation in this vial. Following each steam extraction, the silicone tubing connects the ATRS exhaust line and the first vial was rinsed with 5 mL HPLC grade water (Alfa Aeser) and added to vial 1. Vial 1 was sealed with aluminum foil, labeled, and sent to Exygen with a chain of custody form for PFOA determination. A HPLC grade water (Alfa Aeser) blank and a second blank of HPLC water injected through the syringe were also provided for background PFOA determination.

The pyroprobe used to hold the sample cartridge for gasification was also rinsed using 100 mL HPLC grade water (Alfa Aeser). This water sample was placed in a glass jar, sealed with aluminum foil, labeled, and sent to Exygen with a chain of custody form for PFOA determination. The results of these studies are summarized in Section 3.9.1

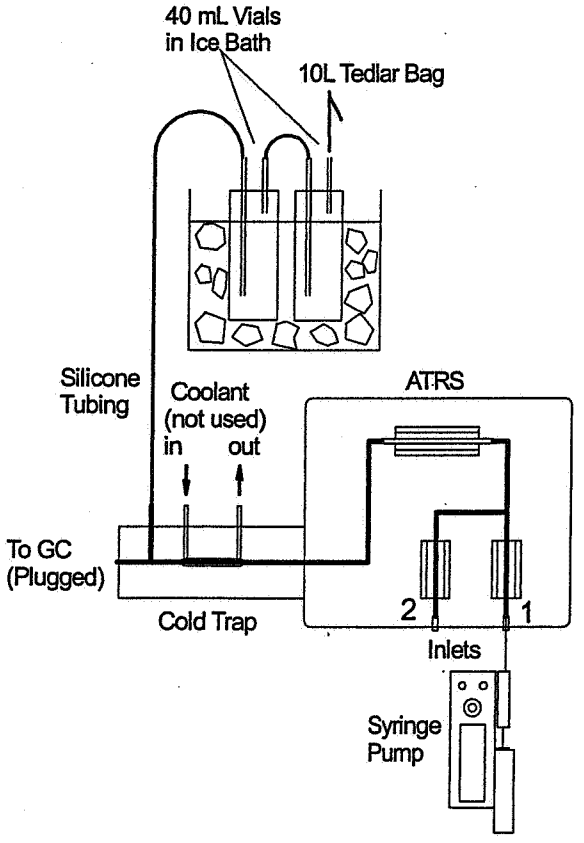


Figure 2.19 Schematic for PFOA Steam Extraction of the ATRS.

2.11.2 PFOA Transport Study - Gas Phase Sampling

Solid PFOA samples were obtained from Oakwood Products, Inc. (West Columbia, SC, Lot No.: 210002) PFOA transport efficiency was determined by comparing the total PFOA ion peak area obtained by direct PFOA injection into the GC/MS with PFOA introduction into Inlet 1 of the ATRS followed by in-line GC/MS analysis. Operational conditions for these two studies were identical and are described in detail below.

For the ATRS tests, the temperature (inlets, transport lines, reactor and the cold trap) were set at 235°C. Synthetic air was used as carrier gas. The total flow rate was set at 33 mL/min (22 mL/min to inlet 1 and 11 mL/min to inlet 2) to maintain the sample residence time in the reactor at 2 sec at 235°C. The same type of sample container used for the previous study (see Section 2.10.1) was used to load PFOA. The pyroprobe temperature was increased from 100 to 300°C at the rate of 200°C/min and held at 300°C for 2 min. After gasification, the system was swept with He for 3 min and the GC temperature programming was started. The GC initial temperature was set at 40°C and held for 1 min. The temperature was increased to 280°C at the rate of 20°C/min and held for 5 min at 280°C.

For the direct GC injection tests, He was used as the carrier flow and the flow rate through the injector was also 33 mL/min. The sample was introduced into the GC injection port using the sample cartridge used for the pyroprobe sample gasification, while the injection port was kept at 40°C. The injection port temperature was then increased to 235°C at a rate of approximately 20°C/min and held for 1 min at 235°C. Then the GC temperature programming was started using the same temperature programming rate used for the ATRS tests.

The PFOA total ion chromatogram peak areas for the two methods were integrated, and the ratio of the peak areas was used as the PFOA transport efficiency through the ATRS. The results are summarized in Section 3.9.2.

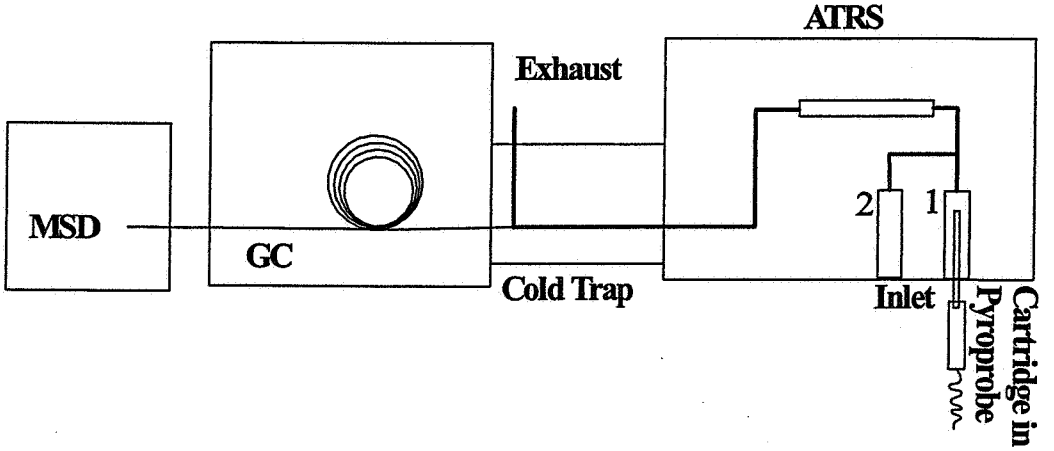


Figure 2.20 Schematic of PFOA Transport Efficiency Test Through the ATRS System.

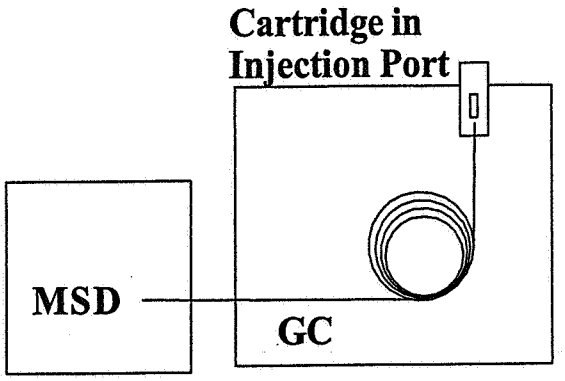


Figure 2.21 Schematic of PFOA Direct Injection to GC Injection Port.

2.12 PFOA Calibration Curve and Detection Limit Study

This study was conducted to identify the actual retention time of PFOA in the GC/MS total ion chromatogram, quantify PFOA if it is formed, and determine the PFOA detection limit using the ATRS with same experimental procedure used for the sample combustion tests. The sample container (2 × 2.5 mm (i.d.×o.d.), 12.5 mm length quartz tubing, CDS Analytical Inc., Oxford, MA) was loaded with 1, 5, 10, 50, and 100 μg PFOA. To load these minute amounts of PFOA, three PFOA solutions with different concentrations were prepared as shown in Table 2.7. The preparation conditions are also summarized in Table 2.7. The results are summarized in Section 3.10.

Table 2.7 Solution Concentration (PFOA in Methanol) and Volume Required to Produce 1, 5, 10, 50, and 100 μg PFOA Injection into ATRS.

Dried Sample Mass (μg)	Solution Used (Concentration) (mg PFOA / mL MeOH[1])	Solution Loaded (μl)	Drying Time (hr)
1	1	1	3
5	1	5	15
10	10	1	3
50	10	5	15
100	100	1	3

[1] MeOH: Methanol

The ATRS, inlets, transport lines, and reactor temperatures were set at 300°C. The total gas flow was set at 29.4 mL/min (19.6 mL/min to inlet 1 and 9.8 mL/min to inlet 2) to maintain a sample residence time in the reactor at 2 sec at 300°C. The pyroprobe temperature was increased from 100 to 300°C at a rate of 200°C/min and held at 300°C for 2 min to gasify PFOA. After gasification, the system was swept with He for 3 min. The gasified PFOA was condensed at the cold trap and released for in-line GC/MS by heating the cold trap to 280°C. The GC conditions were the same as the actual combustion tests in Section 2.4.1. In order to determine if PFOA was lost during solvent evaporation (drying), similarly prepared 500μg samples were weighed before and after drying. Results showed that more than 90% of the PFOA remained during drying. This ca. 10% difference is within the uncertainty of the analytical balance used for the weight measurements.

2.13 Test Matrix and Quality Assurance Procedures

A thermal decomposition profile for each sample was generated from 600°C to $T_{99.9}$. A blank analysis was performed before each combustion test to examine any carryover from previous tests. If any carryover was observed, the reactor assembly, cold trap, and GC column was cleaned at elevated temperature with air (for reactor assembly and trap) and He (for GC column) and a second blank analysis was performed. The cleaning process was continued until no carryover was observed. Blank runs were performed using the same procedure, but without sample insertion. Upon completion of thermal decomposition profiles for each sample, temperatures to perform CO, CO_2, fluoride, and PFOA analyses were determined following a discussion between UDRI and DuPont. CO, CO_2, fluoride, and PFOA sampling and analyses were performed in triplicate at the specified temperature. The test matrices are shown below.

(1) In-line GC/MS Analysis:
All three samples, untreated and treated articles, and fluorinated acrylic polymer were analyzed using the in-line GC/MS system at temperatures from 600°C to $T_{99.9}$ at 50°C increments.
(2) VOC, CO and CO_2 Analyses:
Untreated and treated articles were analyzed using off-line GC/MS for VOC and GC/TCD for CO and CO_2 at the specified temperatures.
(3) PFOA, Fluoride and Chloride Analysis:
Untreated and treated articles were analyzed using ion chromatography and HPLC/MS/MS for PFOA, fluoride, and chloride at specified temperatures.
(4) Additional Study
i) XPS Analysis: Sample cartridge used for treated article combustion.
ii) Telomer B Alcohol Analysis: Telomer B Alcohol combustion at 200 and 600°C.
iii) PFOA Absorption Test at 170°C.
iv) PFOA Transport Test at 170 and 300°C.
v) PFOA Steam Extraction at 300°C
vi) PFOA Calibration Curve and Detection Limit Study at 300°C

2.14 Quality Assurance Narrative Statement

This program involved conducting thermal decomposition tests on a fluorinated acrylic polymer, an article treated with the polymer, and an untreated article provided by DuPont. All analysis and handling of data fully conformed to ANSI/ASQC E4 requirements (ASQ, 1994). All analysis techniques were performed with the appropriate ASTM or US-EPA standard methods. Any specialized, non-standard analytical techniques used fully developed SOPs which have been incorporated into prior EPA-approved Quality Assurance Project Plans (US-EPA, 2000).

1. Study Design: The overall study design is described in Section 2 of this report.

2. Sample Handling and Custody: Chain of custody procedures previously developed under US-EPA Quality Assurance Program Plans (QAPPs) were followed during this program. All samples were composed of purchased chemicals of known purity or samples provided by DuPont. All samples, including any hazardous chemicals, were received, labeled and logged, with hazardous materials placed into a pre-existing Hazardous Materials Handling Facility. Samples were not removed from storage except as labeled prepared samples for immediate study.

3. Sample Analysis: Only samples of known purity were purchased. All analysis techniques were performed in compliance with appropriate standard methods. Any specialized, non-standard

analytical techniques have fully developed SOPs that were followed and which have been incorporated into prior EPA-approved QAPPs.

4. Calibration and Performance Analysis of Sampling and Analytical Methods: All of the measurement and analytical equipment used in this program are commercially available and calibrated and maintained in accordance with the manufacturer's SOPs. Quantitative analysis of samples was performed using established GC/MS methods including the use of certified internal standards as needed.

5. ATRS Operation: Known amounts of the samples were gasified with 85% excess air. The mean gas-phase residence time in the reactor was maintained at 2 sec. The reactor and transport line temperature and carrier flow rate were monitored and logged before and after the experiments. The reactor temperature was kept within ±1°C of the set temperature for most cases and ±2°C for few cases. The flow rate was kept within ±0.2 mL/min of the set flow for all cases.

6. Data Reduction and Reporting: Tables of calibration data were furnished, along with graphs of reduced data. Standard deviations, regression coefficients, and other statistical measures of data quality were calculated from linear or nonlinear regression analyses of data. All data are subject to internal review by the project leader

7. Intended Use of the Data: The data generated in this study were used to provide guidance as to the temperature required to destroy the parent material with an efficiency of >99.9% and all organic products to an equivalent level with a mean exposure time of 2 sec and a level of excess air of no lower than 85%. The data also provided guidance as to the identification of organic products and the temperature required to destroy them.

8. Evaluation of the Success of the Project: The success of the project will be indicated by our ability to determine the temperature required to destroy the parent material with an efficiency of >99.9% and all organic products to an equivalent level with a mean exposure time of 2 sec and a level of excess air of no lower than 85%.

9. Reviews of the Study Plan: The study plan and the proposed analytical methods were prepared by the project leader and his research team within the Environmental Engineering Group. It is common practice for external review by the sponsor's technical representative or designated alternate.

3. Experimental Results

3.1 In-line GC/MS Analysis and 99.9% Destruction Temperature Determination

Thermal decomposition profiles for the untreated and treated articles and fluorinated acrylic polymer were generated using the ATRS with in-line GC/MS analysis. The thermal decomposition profile and extracted ion chromatograms at each temperature for each sample are presented in this section. Raw data for all experiments are presented in Appendix A.

3.1.1 Untreated Article

Ions 122 (benzoic acid) and 149 (terephthalic acid derivative), which are the major ions of the untreated article at the temperature of complete gasification, were used to determine the thermal decomposition profile. Table 3.1 shows total ion counts and summation of ions 122 and 149. Both ions disappear at 725 and 700°C, respectively. The analysis was repeated at 750°C to ensure complete sample destruction. The total ion counts were also normalized by gasified sample mass and the relative degradation was calculated. $T_{99.9}$ was obtained at 725°C. Figure 3.1 shows the degradation profile of the untreated article. Figures 3.2 and 3.3 show extracted ions 122 and 149 for the untreated article at 600, 650, 700, and 725°C, respectively. Ions 122 and 149 were also extracted for combustion at 1000°C to ensure that these compounds were not reformed at higher temperature. Figure 3.4 shows the results. Only a background signal was observed, and there is no indication of reformation of these compounds.

Table 3.1 Major Ion Counts of the Untreated Article.

Temp (°C)	Ion 122	Ion 149	Total	Mass (mg)	Normalized By Mass	Relative %
600	2.31E+08	4.48E+07	2.76E+08	1.11	2.48E+08	100
650	1.82E+08	1.31E+06	1.83E+08	1.01	1.81E+08	72.95
700	4.53E+07	0.00E+00	4.53E+07	1.02	4.44E+07	17.86
725	0.00E+00	0.00E+00	0.00E+00	1.00	0.00E+00	0.00
750	0.00E+00	0.00E+00	0.00E+00	0.97	0.00E+00	0.00
750	0.00E+00	0.00E+00	0.00E+00	1.04	0.00E+00	0.00

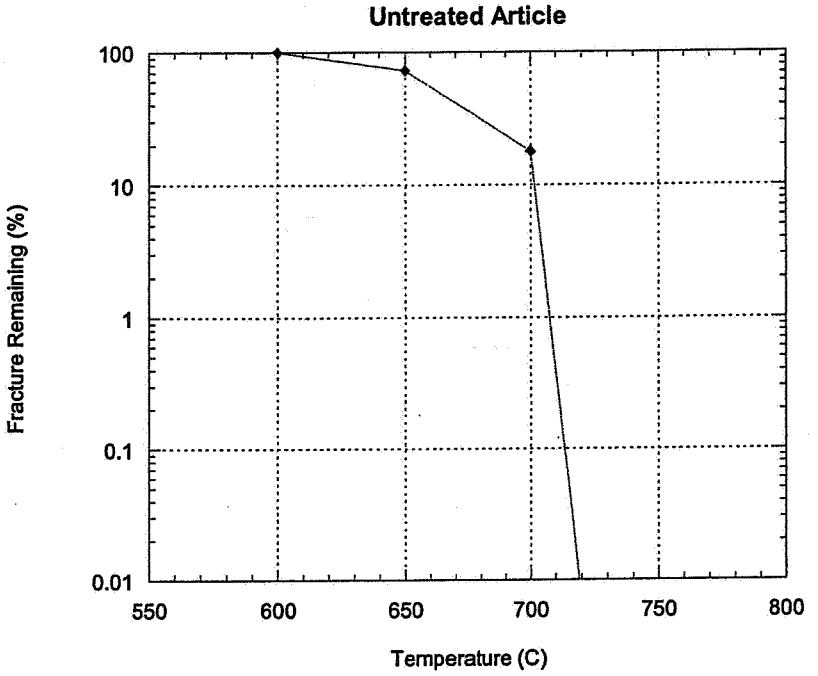


Figure 3.1 Untreated Article Thermal Destruction Profile Normalized by Sample Mass.

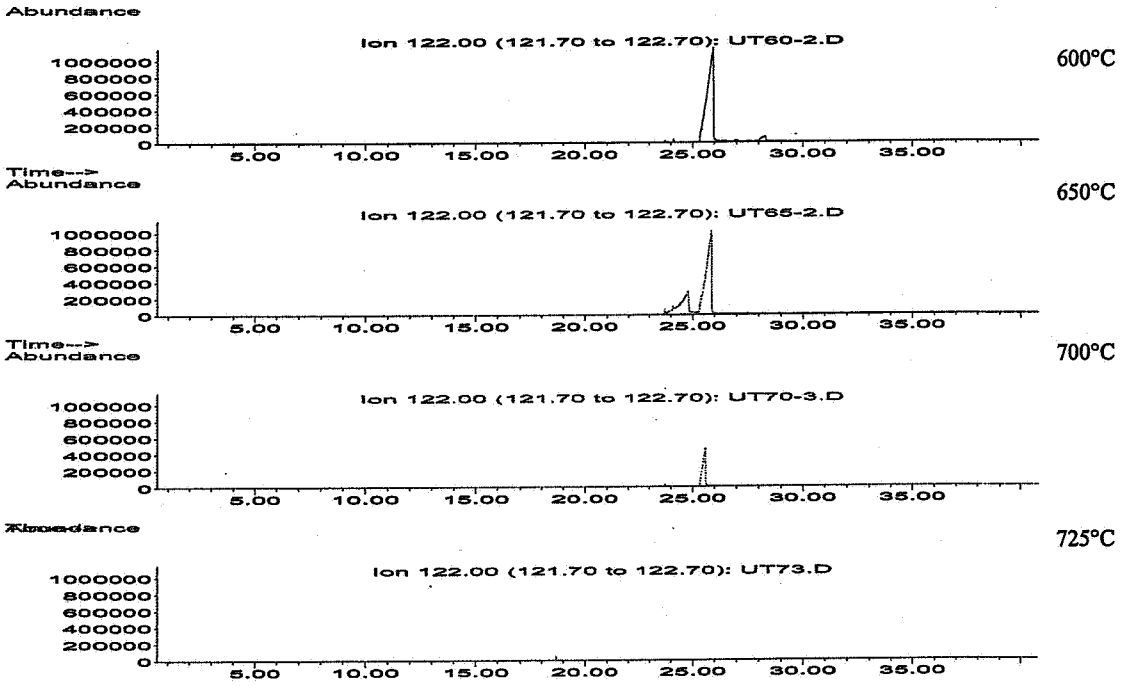


Figure 3.2 Extracted Ion 122 (benzoic acid) for Untreated Article at 600, 650, 700, and 725°C.

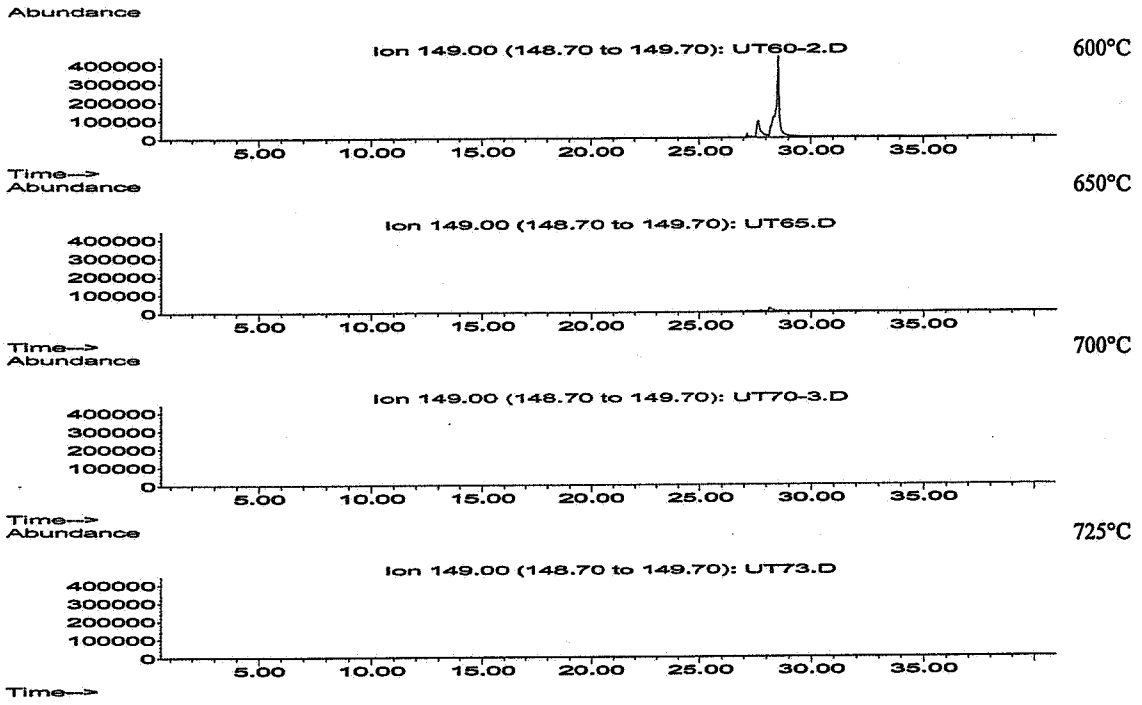


Figure 3.3 Extracted Ion 149 (terphthalic acid derivative) for Untreated Article at 600, 650, 700, and 725°C.

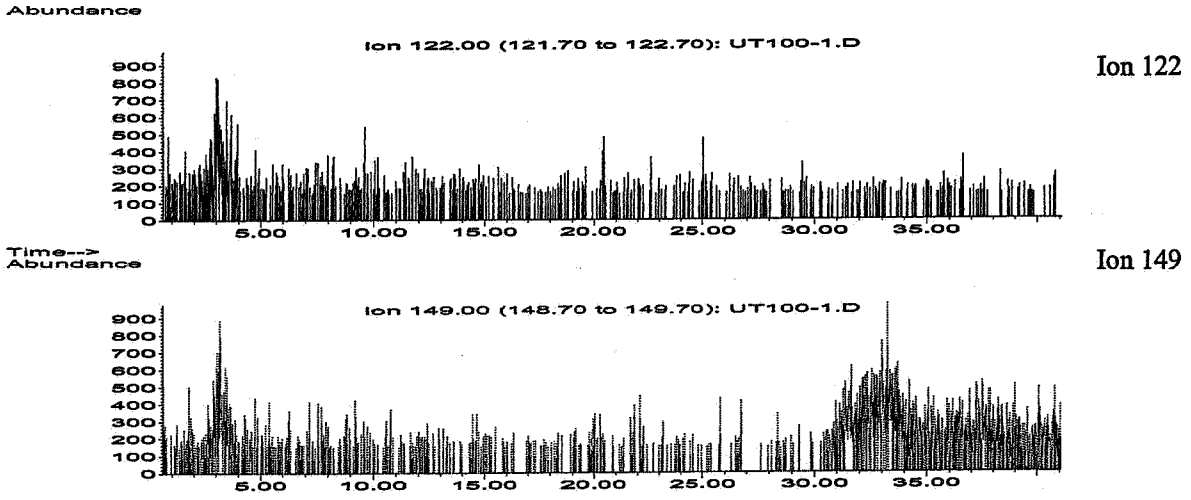


Figure 3.4 Extracted Ion 122 (benzoic acid) and 149 (terephthalic acid derivative) for Untreated Article Combustion at 1000°C.

3.1.2 Treated Article

Ions 122 and 149 were also used to determine the thermal decomposition profile of the treated article. Table 3.2 shows total ion counts and a summation of ions 122 and 149. Ions 122 and 149 disappear at 700 and 725°C, respectively. The analysis was repeated at 750°C to ensure complete sample destruction. $T_{99.9}$ was obtained at 725°C. Figure 3.5 shows the degradation profile of the treated article. Figures 3.6 and 3.7 show the extracted ions 122 and 149 for the treated article at 600, 650, 700, and 725°C, respectively. Ions for fluorinated species fragments (69 for $\bullet CF_3$, 119 for $\bullet CF_2CF_3$, and 131 for $\bullet CF_2CF{=}CF_2$) were also extracted and are shown in Figures 3.8, 3.9, and 3.10, respectively. Ion 69 was observed even at 725°C, but the amount was very small. Ions 119 and 131 were destroyed at 725°C. No other fluorinated species fragment was observed for the treated article combustion test. Ions 122 and 149 were extracted for the combustion at 1000°C to ensure these compounds were not reformed at higher temperature. Figure 3.11 shows the results. Only a background signal was observed.

Table 3.2 Major Ion Counts of the Treated Article.

Temp (C)	Ion 122	Ion 149	Total	Mass (mg)	Normalized by Mass	Relative %
600	2.80E+08	5.43E+07	3.34E+08	1.22	2.74E+08	100
650	2.38E+08	6.15E+06	2.44E+08	1.25	1.95E+08	71.27
700	1.49E+06	0.00E+00	1.49E+06	1.22	1.22E+06	0.45
725	0.00E+00	0.00E+00	0.00E+00	1.23	0.00E+00	0.00
750	0.00E+00	0.00E+00	0.00E+00	1.24	0.00E+00	0.00
750	0.00E+00	0.00E+00	0.00E+00	1.23	0.00E+00	0.00

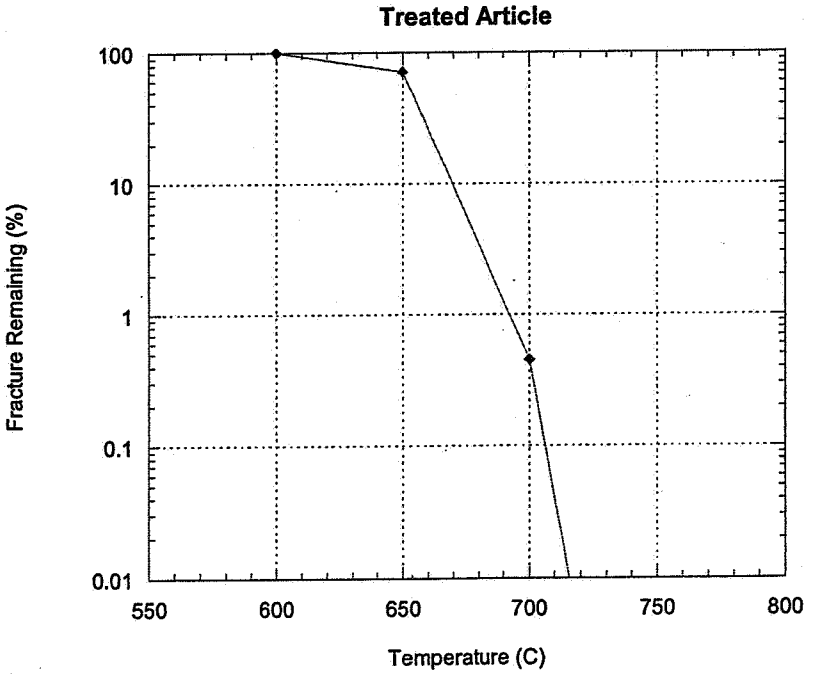


Figure 3.5 Treated Article Thermal Destruction Profile Normalized by Sample Mass.

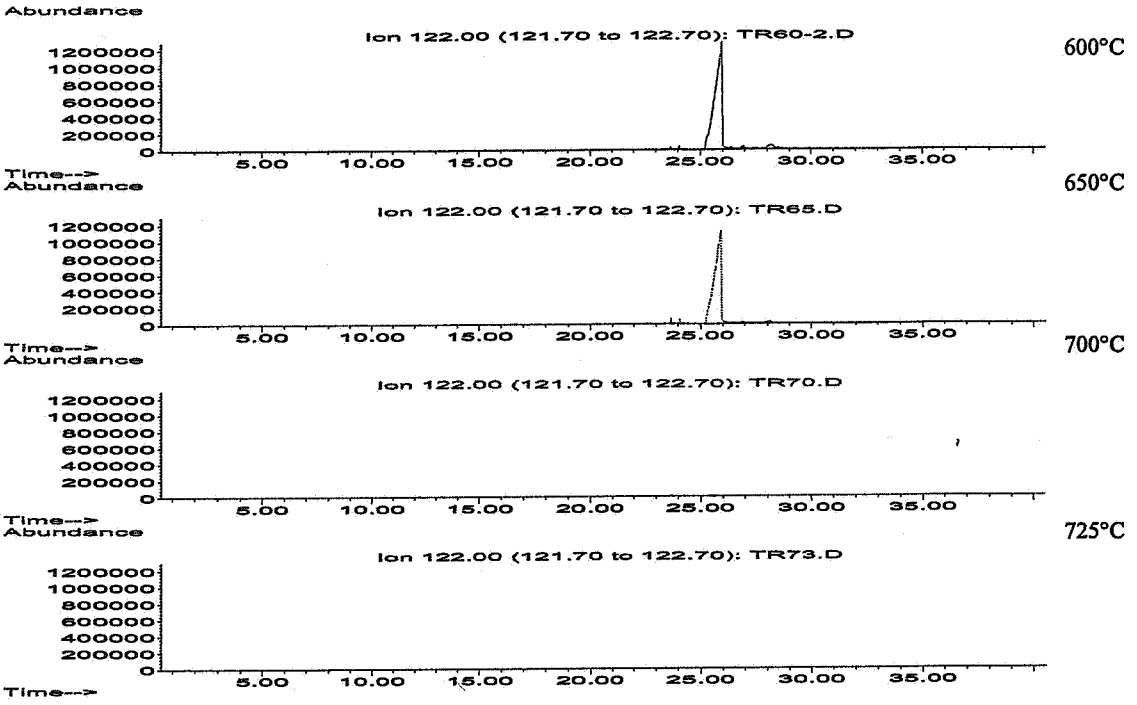


Figure 3.6 Extracted Ion 122 (benzoic acid) for Treated Article at 600, 650, 700, and 725°C.

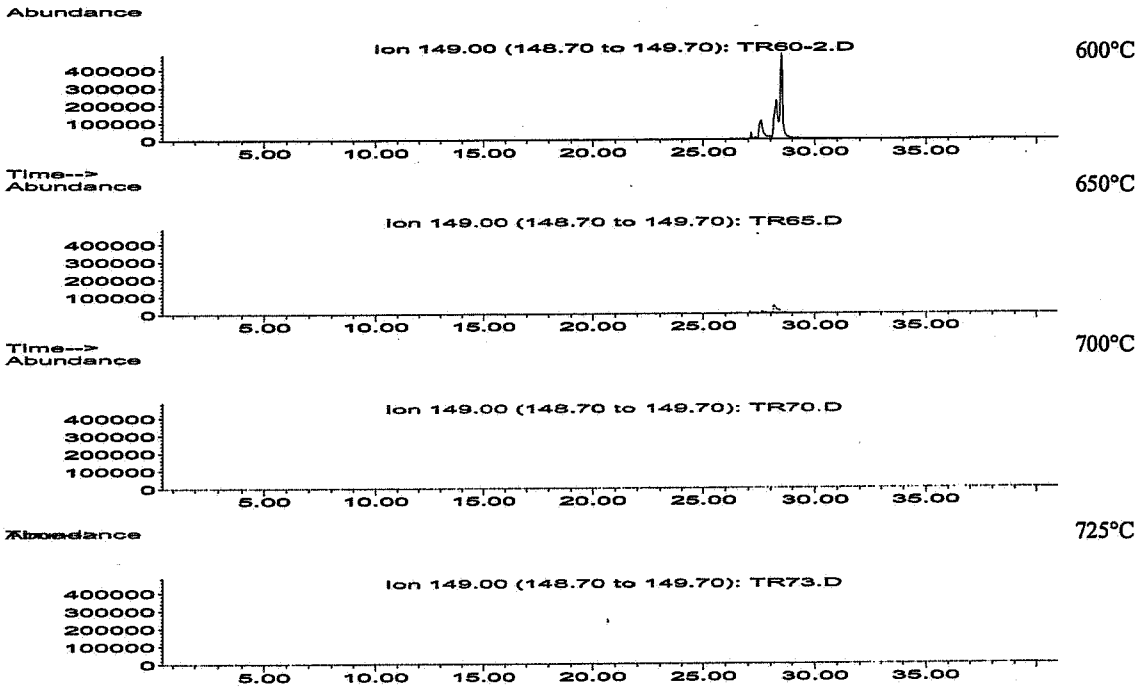


Figure 3.7 Extracted 149 (terphthalic acid derivative) for Treated Article at 600, 650, 700, and 725°C.

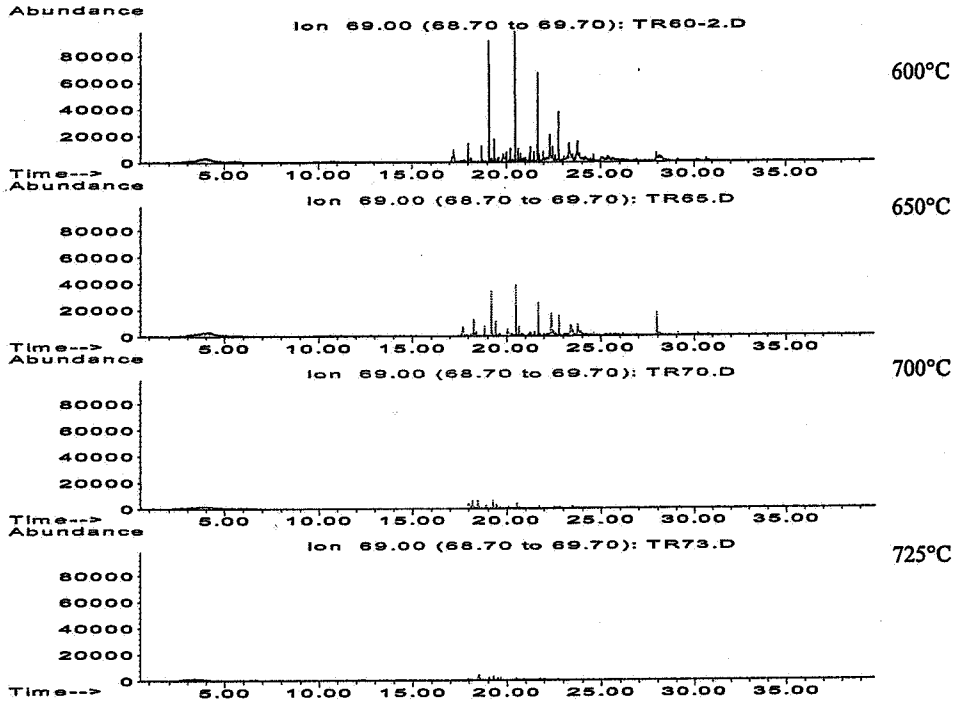


Figure 3.8 Extracted Ion Count 69 ($\bullet CF_3$) for Treated Article at 600, 650, 700, and 725°C.

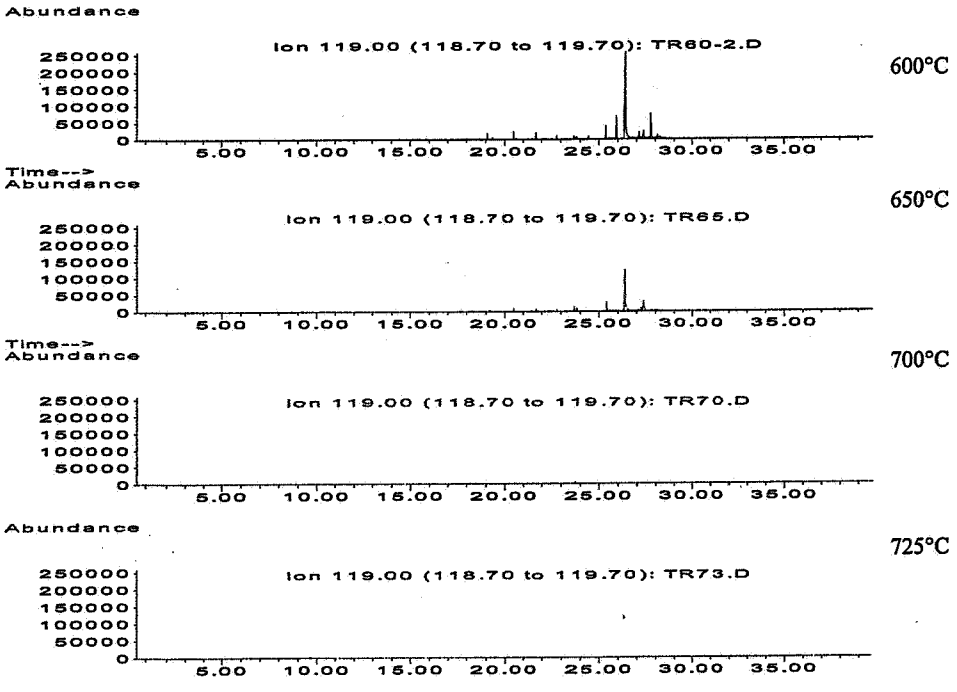


Figure 3.9 Extracted Ion 119 ($\bullet CF_2CF_3$) for Treated Article at 600, 650, 700, and 725°C.

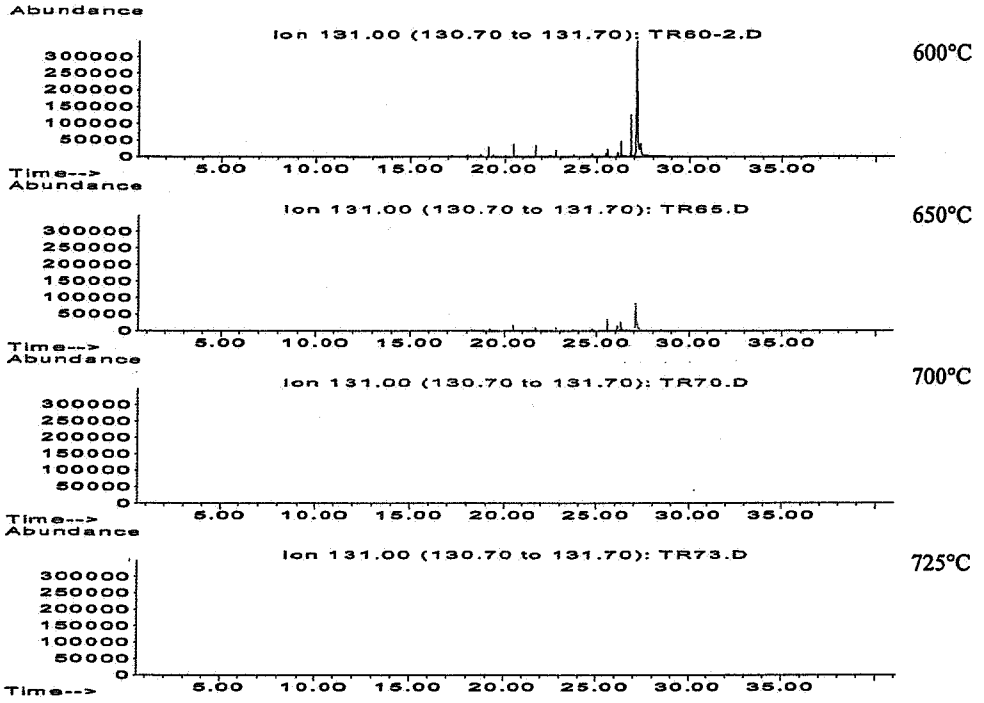


Figure 3.10 Extracted Ion 131 ($\bullet CF_2CF{=}CF_2$) for Treated Article at 600, 650, 700, and 725°C.

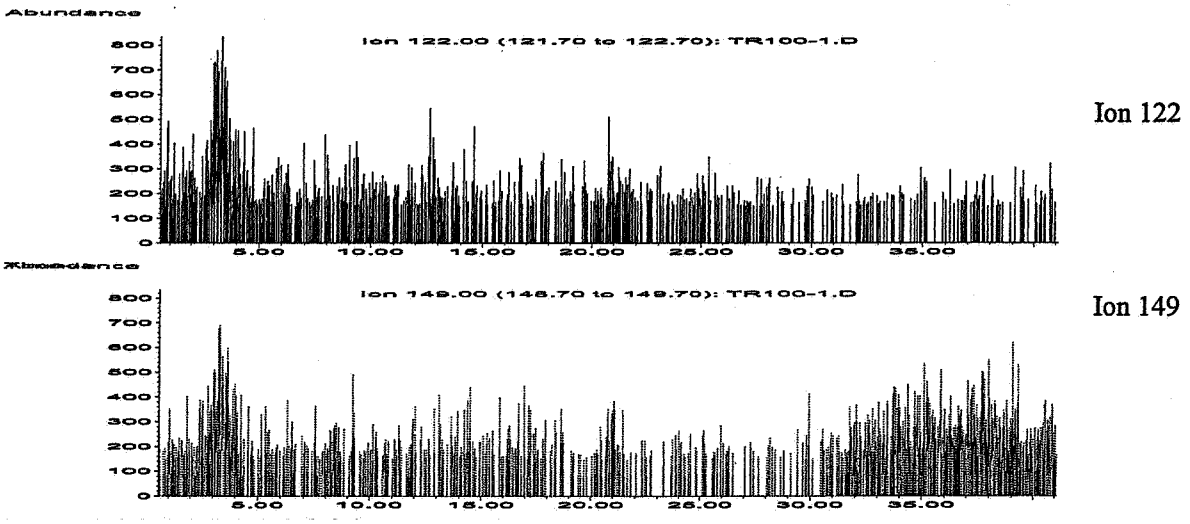


Figure 3.11 Extracted Ion 122 (benzoic acid) and 149 (terephthalic acid derivative) for Treated Article Combustion at 1000°C.

3.1.3 Fluorinated Acrylic Polymer

Ions 69 ($\bullet CF_3$) and 77 ($\bullet CF_2CH{=}CH_2$), which are the major ions from the gasification of the fluorinated acrylic polymer, were used to determine the thermal decomposition profile. Table 3.3 shows total ion counts and a summation of ions 69 and 77. Ions 69 and 77 still exist at 1000°C, but the relative amount remaining is ≤0.1%. The analysis was repeated at 1000°C to ensure 99.9% sample destruction. The total ion counts were also normalized by gasified sample mass and relative degradation rate was calculated. $T_{99.9}$ was obtained at 1000°C. Figure 3.12 shows the degradation profile of the fluorinated acrylic polymer, and Figures 3.13 and 3.14 show the extracted Ion 69 at low (600 ~ 800°C) and high (850 ~ 1000°C) temperatures, respectively. Figures 3.15 and 3.16 show the extracted ion 77 ($\bullet CF_2CH{=}CH_2$) at low and high temperatures, respectively. Figures 3.17 and 3.18 show extracted ion 119 ($\bullet CF_2CF_3$) at low and high temperatures, respectively. Figures 3.19 and 3.20 show the extracted ions 131 ($\bullet CF_2CF{=}CF_2$) and 169 ($\bullet CF_2CF_2CF_3$), respectively. All ions correspond to the fluorinated compound, with the exception that ion 69 ($\bullet CF_3$) is relatively small compared to ion 77($\bullet CF_2CH{=}CH_2$) , and these ions are negligible at combustion temperatures over 800°C.

Table 3.3 Major Ion Counts of Fluorinated Acrylic Polymers.

Temp (C)	Ion 69	Ion 77	Total	Mass (mg)	Normalized by Mass	Relative %
600	1.44E+09	2.08E+09	3.51E+09	1.60	2.20E+09	100.00
650	1.21E+09	1.15E+09	2.36E+09	1.69	1.40E+09	63.58
700	1.02E+09	2.24E+08	1.25E+09	1.68	7.43E+08	33.81
750	8.13E+08	1.44E+07	8.27E+08	1.62	5.10E+08	23.24
800	6.80E+08	1.50E+07	6.95E+08	1.63	4.26E+08	19.41
850	3.29E+08	7.45E+06	3.36E+08	1.62	2.07E+08	9.45
900	1.14E+08	5.13E+06	1.19E+08	1.63	7.30E+07	3.32
950	4.79E+07	4.62E+06	5.25E+07	1.58	3.32E+07	1.51
1000	1.13E+06	1.54E+06	2.68E+06	1.61	1.66E+06	0.08
1000	4.43E+05	3.61E+06	4.06E+06	1.61	2.52E+06	0.11
1000	2.12E+06	1.08E+06	3.21E+06	1.58	2.03E+06	0.09

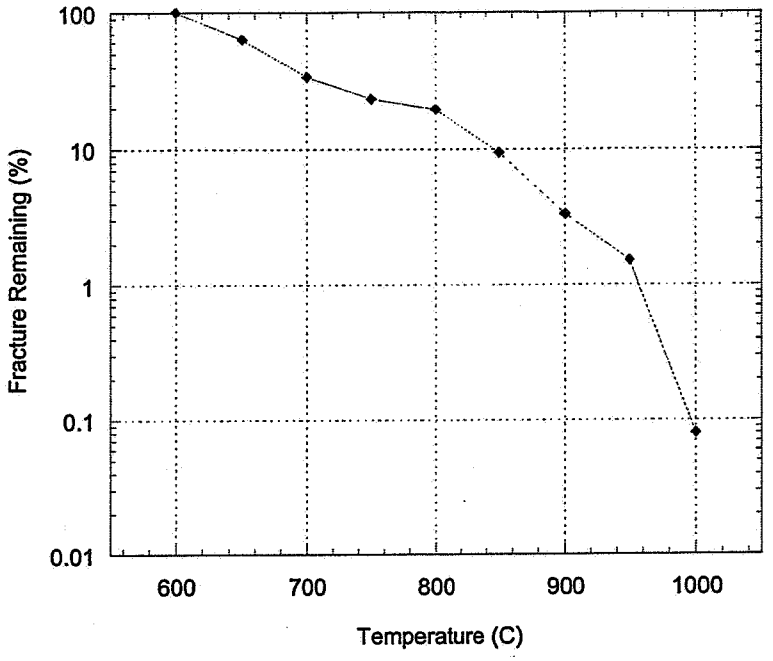


Figure 3.12 Fluorinated Acrylic Polymer Thermal Destruction Profile.

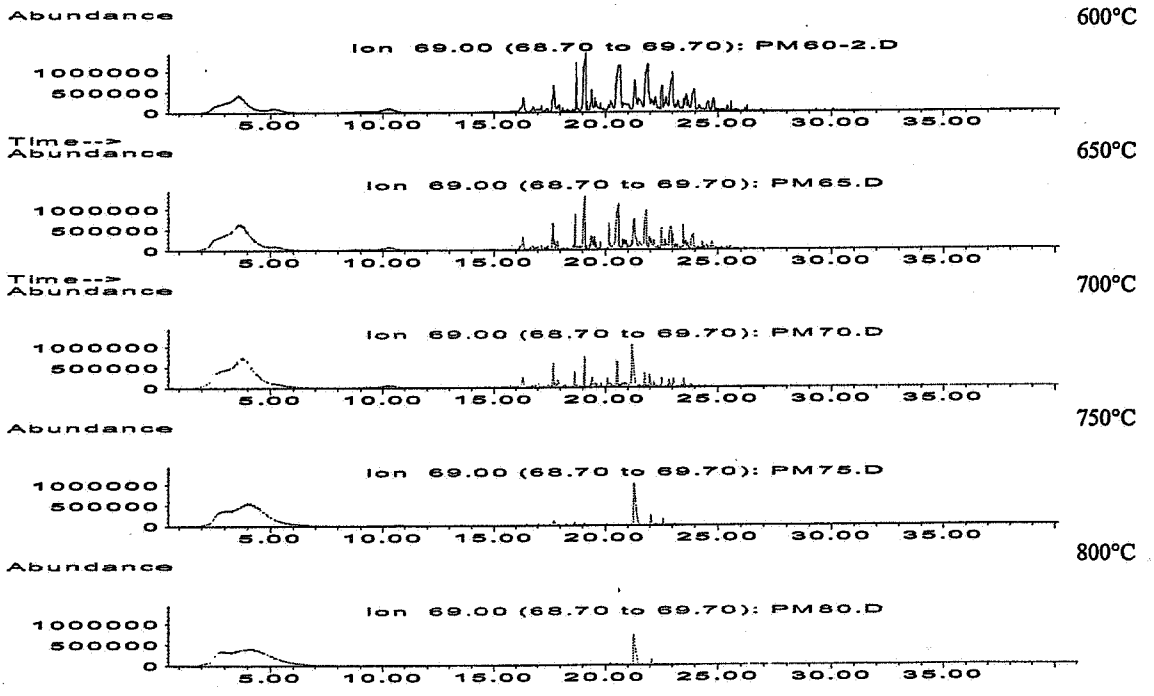


Figure 3.13 Extracted Ion 69 ($\bullet CF_3$) for Fluorinated Acrylic Polymer at 600, 650, 700, 750, and 800°C.

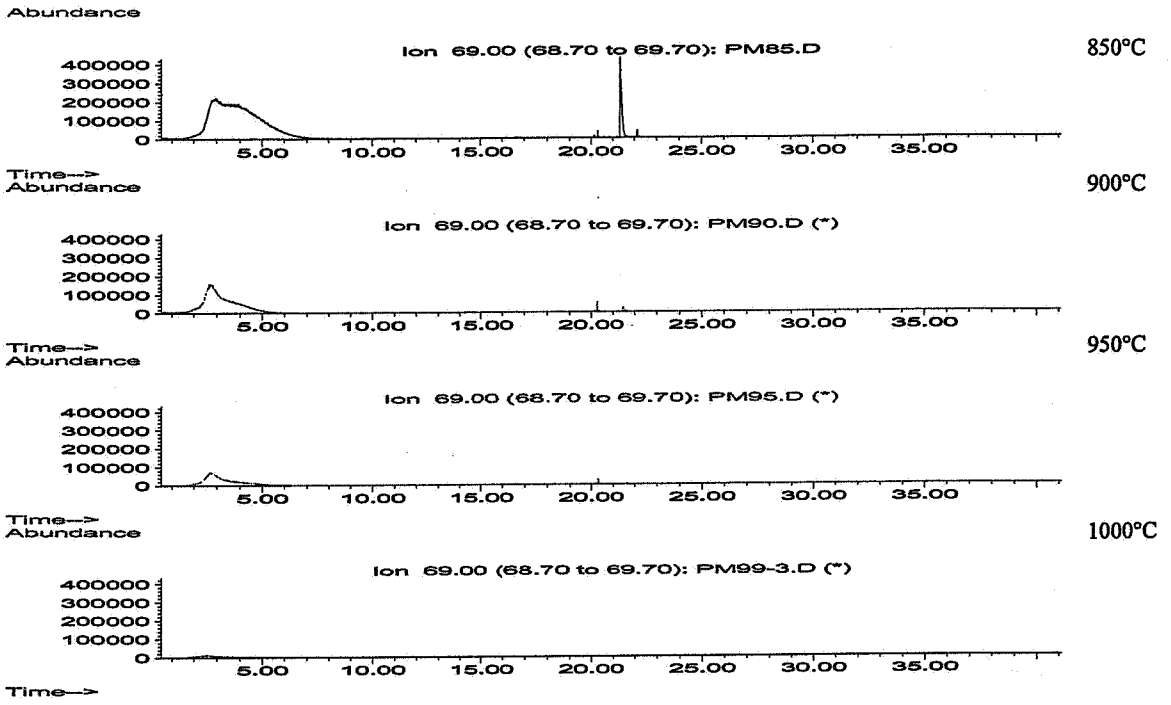


Figure 3.14 Extracted Ion 69 ($\bullet CF_3$) for Fluorinated Acrylic Polymer at 850, 900, 950, and 1000°C.

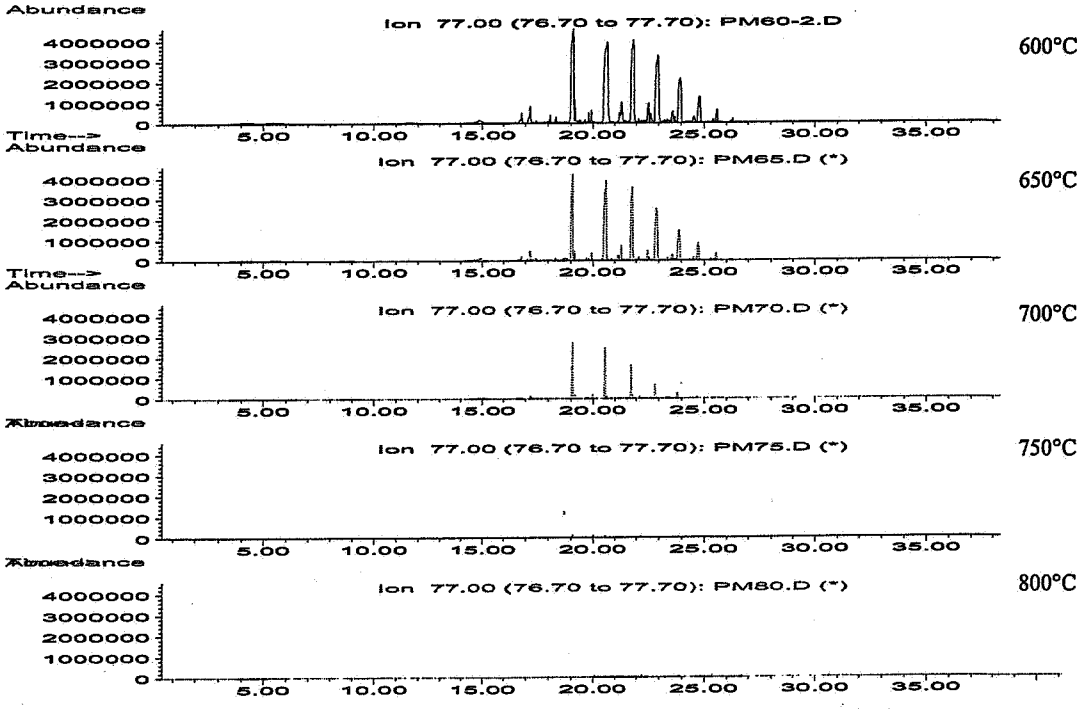


Figure 3.15 Extracted Ion 77($\bullet CF_2CH{=}CH_2$) for Fluorinated Acrylic Polymer at 600, 650, 700, 750, and 800°C.

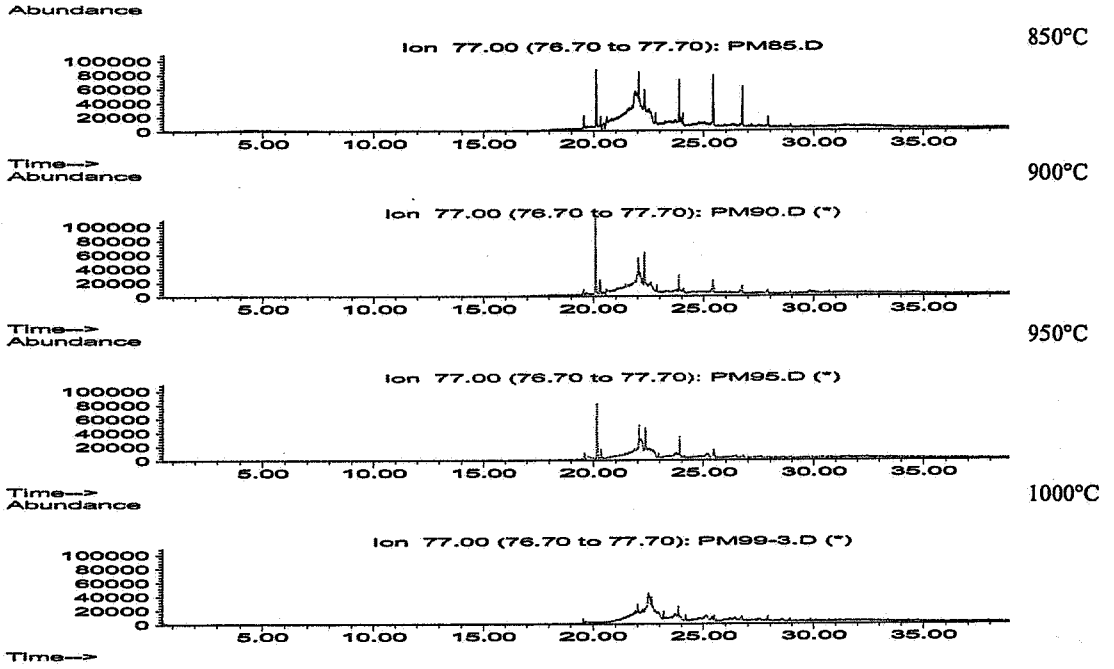


Figure 3.16 Extracted Ion 77 ($\bullet CF_2CH{=}CH_2$) for Fluorinated Acrylic Polymer at 850, 900, 950 and 1000°C.

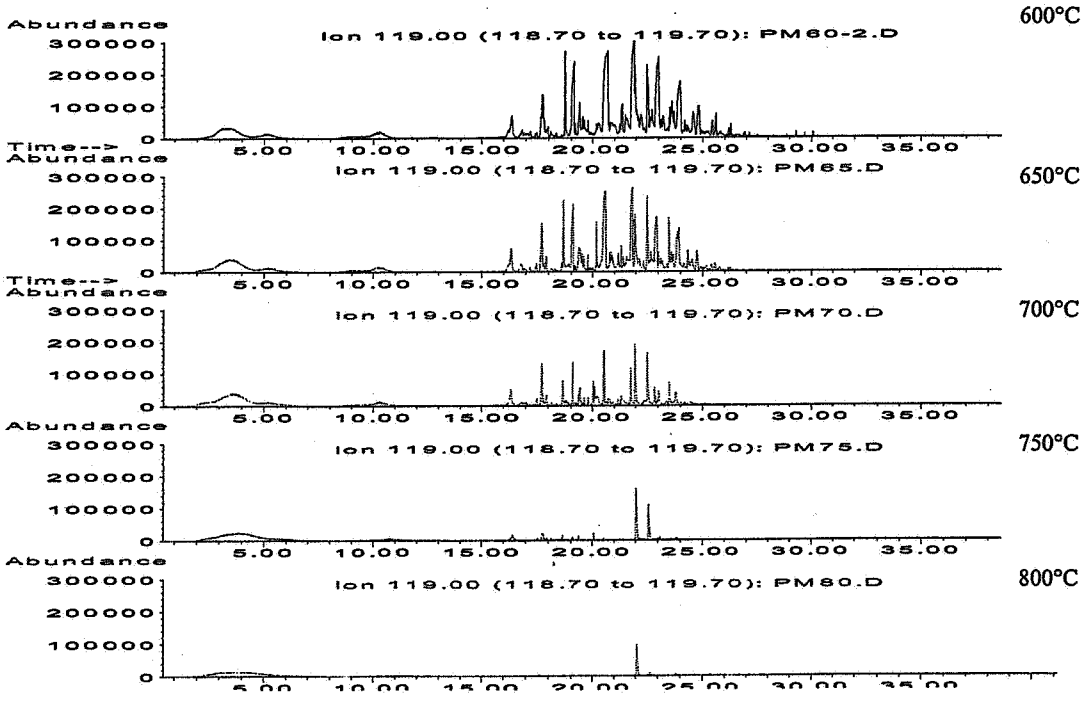


Figure 3.17 Extracted Ion 119($\bullet CF_2CF_3$) for Fluorinated Acrylic Polymer at 600, 650, 700, 750, and 800°C.

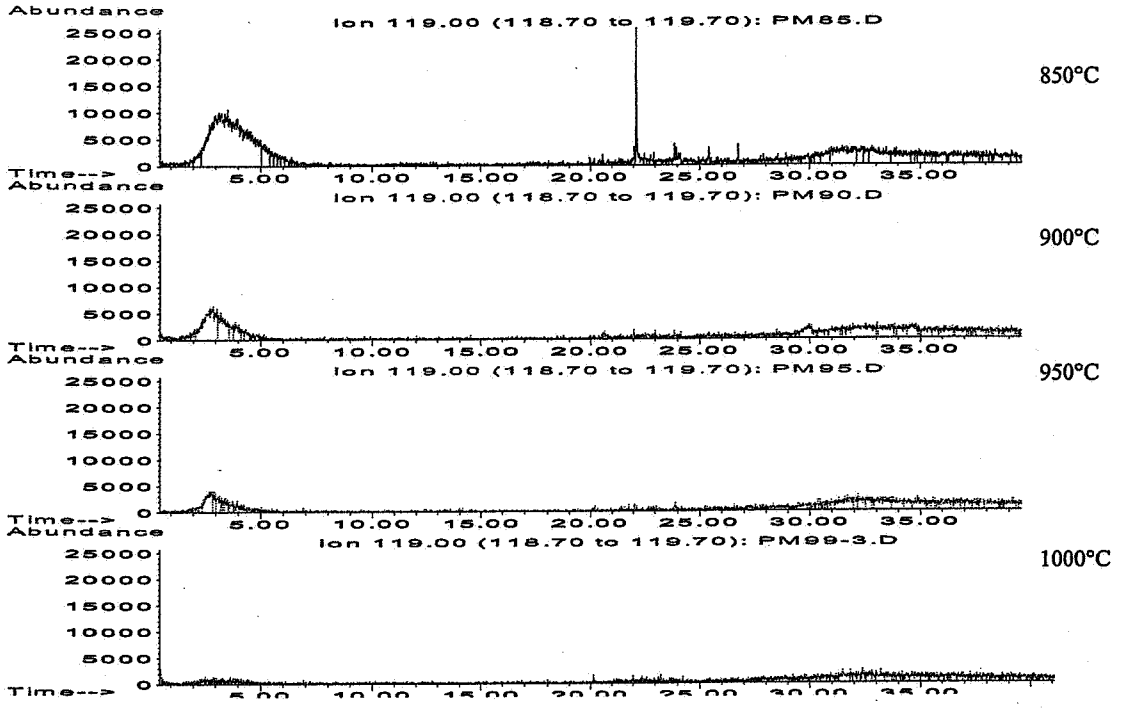


Figure 3.18 Extracted Ion 119($\bullet CF_2CF_3$) for Fluorinated Acrylic Polymer at 850, 900, 950, and 1000°C.

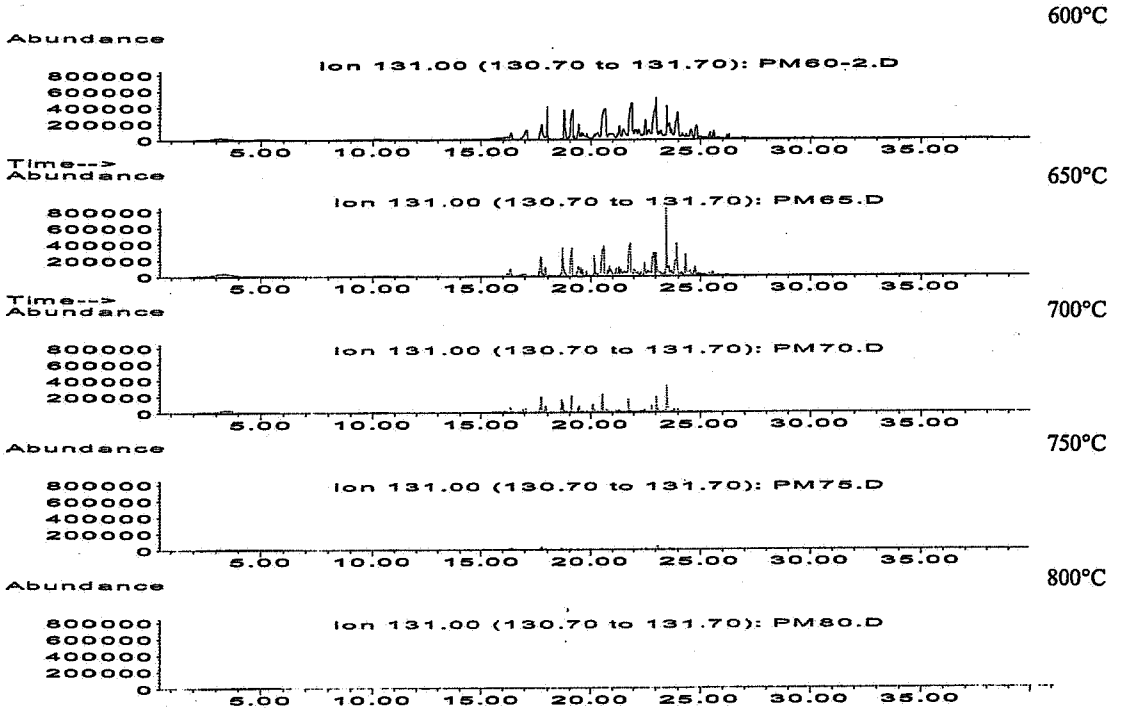


Figure 3.19 Extracted Ion 131($\bullet CF_2CF{=}CF_2$) for Fluorinated Acrylic Polymer at 600, 650, 700, 750, and 800°C.

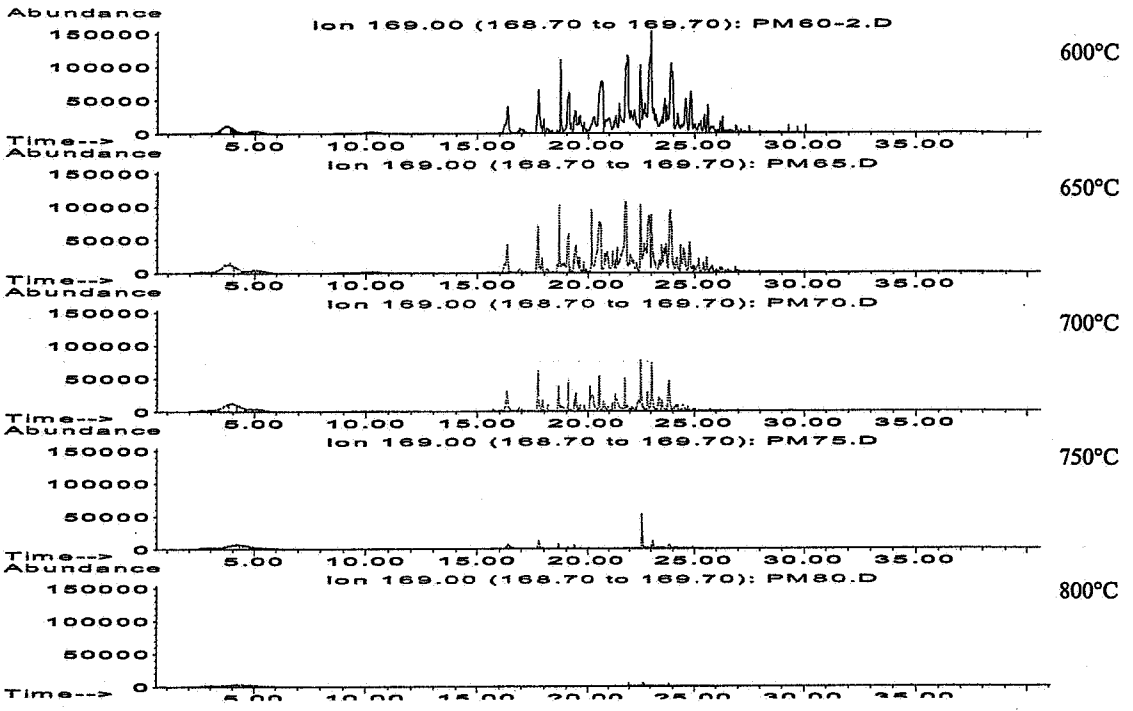


Figure 3.20 Extracted Ion 169($\bullet CF_2CF_2CF_3$) for Fluorinated Acrylic Polymer at 600, 650, 700, 750, and 800°C.

3.2 Treated & Untreated Articles: PFOA, Fluoride, and Chloride Determination at 1000°C

The reactor effluent from combustion tests of the treated and untreated articles at a temperature of 1000°C was analyzed for PFOA, fluoride, and chloride. No PFOA, fluoride, and chloride were detected. The detection limit of PFOA, fluoride, and chloride were 10 ng/L, 10 µg/L, and 40 µg/L, respectively. The net amount of samples gasified is tabulated in Table 3.4. Raw data including the report provided by Exygen are provided in Appendix B.

Fluoride and chloride analyses for treated article combustion at 1000°C were also conducted at UDRI to provide verification of the prior results provided by Exygen. The analyses were conducted using flow injection analysis colorimetry (QuikChem Method 10-109-12-2-A and 10-117-07-1-C for fluoride and chloride, respectively. See Appendix G for detail). The detection limits were 100 µg/L for both fluoride and chloride. No detectable amounts of fluoride and chloride were observed. The net amount of sample gasified is tabulated in Table 3.4 and the analytical results are shown in Appendix B.

Table 3.4 Gasified Sample Masses.

Sample Name	Gasified Mass (mg)
Untreated article 1 analyzed at Exygen	2.13
Untreated article 2 analyzed at Exygen	2.05
Untreated article 3 analyzed at Exygen	2.13
Treated article 1 analyzed at Exygen	2.54
Treated article 2 analyzed at Exygen	2.66
Treated article 3 analyzed at Exygen	2.47
Treated article 1 analyzed at UDRI	2.47
Treated article 2 analyzed at UDRI	2.49

3.3 SiF_4 Analysis from Fluorinated Acrylic Polymer Combustion

Silicon tetrafluoride (SiF_4) is not formed by sample combustion but through interaction between hydrogen fluoride (HF) and the reactor surfaces (fused silica). SiF_4 demonstrates HF formation from fluorinated acrylic polymer combustion. Figures 3.23 and 3.24 show the integrated peak area of extracted ion 85 for fluorinated acrylic polymer combustion tests at low temperatures (600 to 800°C) and high temperatures (850 to 1000°C), respectively. A significant amount of SiF_4 was observed for the fluorinated acrylic polymer combustion tests, and the integrated peak area increased with temperature. Table 3.5 and Figure 3.25 show temperature vs. integrated peak area normalized by gasified sample mass. The peak area increases with a slight S-shape, except at 850°C. Because the pyroprobe temperature programming for the gasification is identical throughout the fluorinated acrylic polymer combustion tests, it is clear that HF formed by combustion reacted with fused silica on the reactor surfaces to form SiF_4.

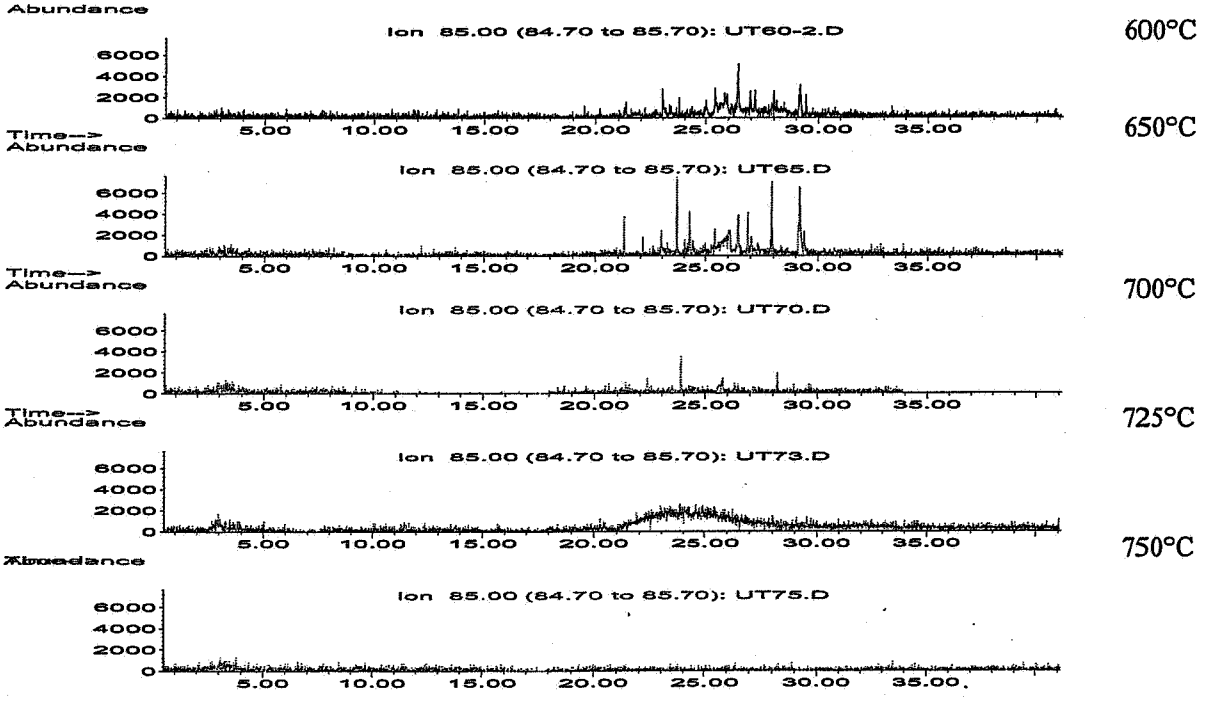


Figure 3.21 Extracted Ion 85 (SiF_3) for Untreated Article at 600, 650, 700, 725, and 750°C.

Figures 3.22 and 3.23 show the integrated peak areas of SiF_4 extracted ion 85, for untreated and treated article combustion tests at 600, 650, 700, 725, and 750°C, respectively. No significant ion 85 peak was observed for these materials, consistent with the low levels of F present in these materials.

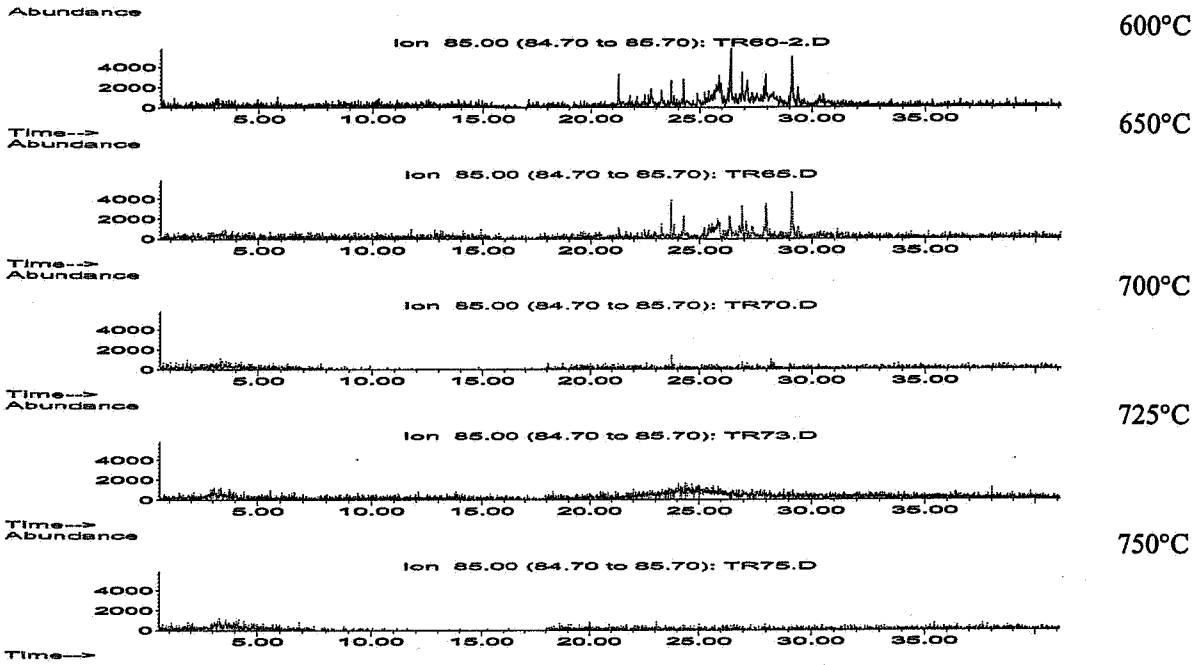


Figure 3.22 Extracted Ion 85 (SiF_3) for Treated Article at 600, 650, 700, 725, and 750°C.

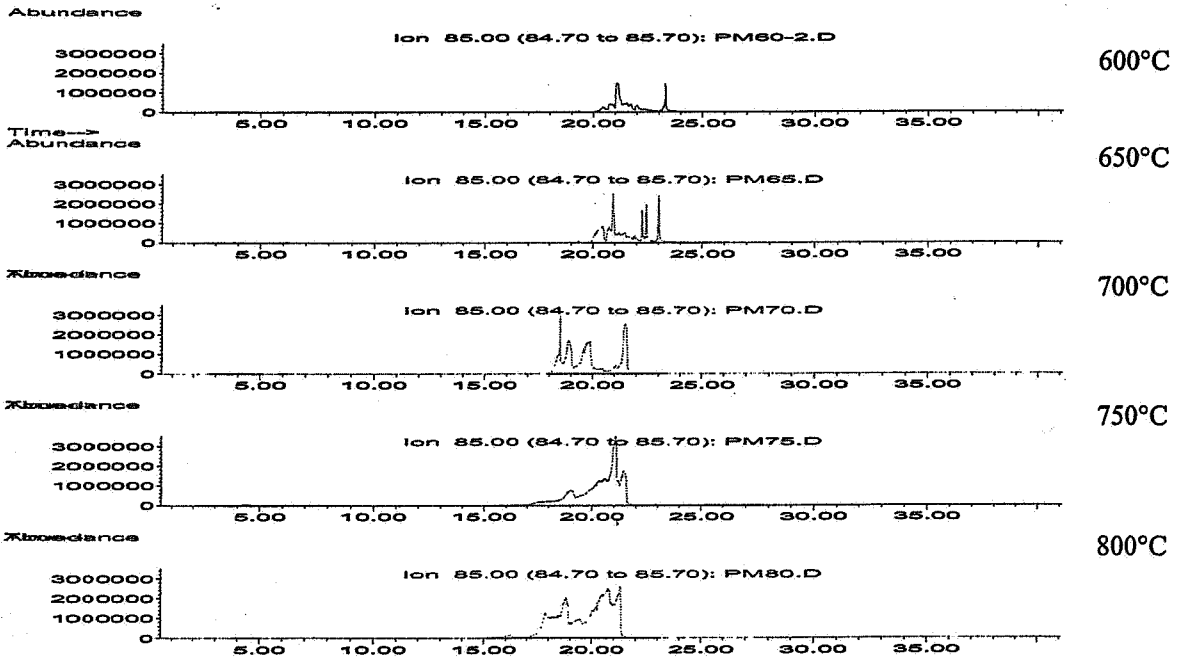


Figure 3.23 Extracted Ion 85 (SiF_3) for Fluorinated Acrylic Polymer at 600, 650, 700, 750, and 800°C.

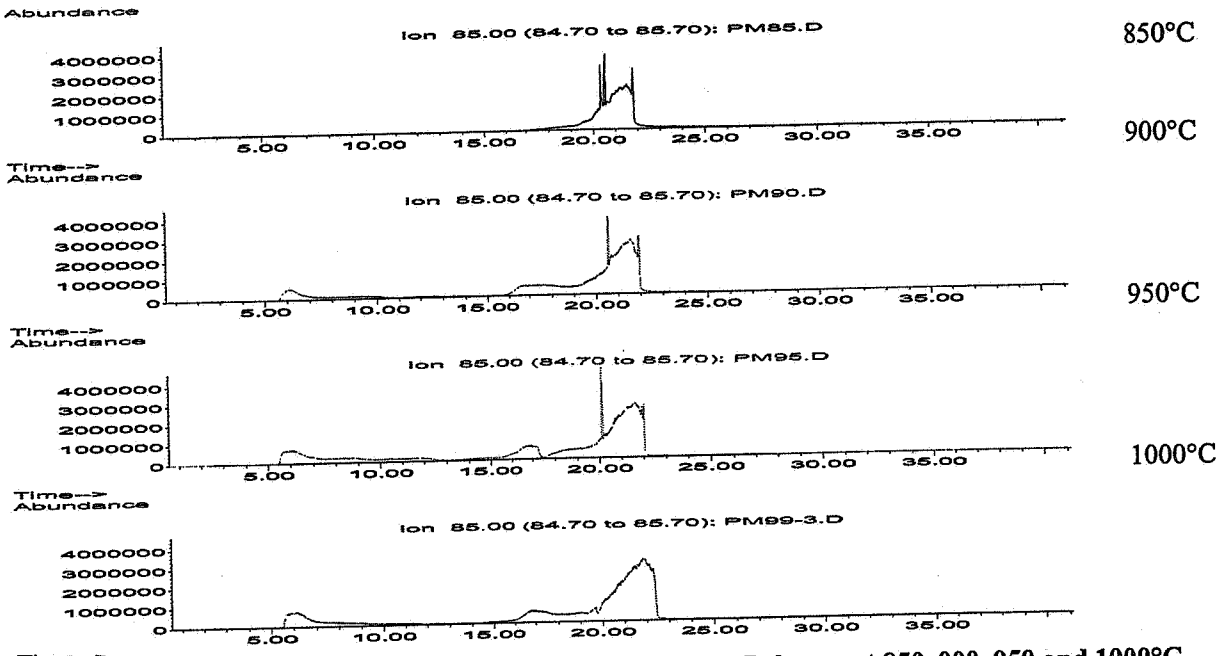


Figure 3.24 Extracted Ion 85 (SiF_3) for Fluorinated Acrylic Polymer at 850, 900, 950 and 1000°C.

Table 3.5 Integrated Peak Area of Ion 85 (SiF_3) Normalized by Mass for the Fluorinated Acrylic Polymer.

Temperature (°C)	Peak Area	Mass (mg)	Peak Area Normalized by Mass
600	5.85E+08	1.60	3.66E+08
650	9.07E+08	1.69	5.36E+08
700	1.51E+09	1.68	8.98E+08
750	2.13E+09	1.62	1.32E+09
800	3.27E+09	1.63	2.00E+09
850	2.43E+09	1.62	1.50E+09
900	4.30E+09	1.63	2.64E+09
950	4.93E+09	1.58	3.12E+09
1000	5.28E+09	1.61	3.28E+09

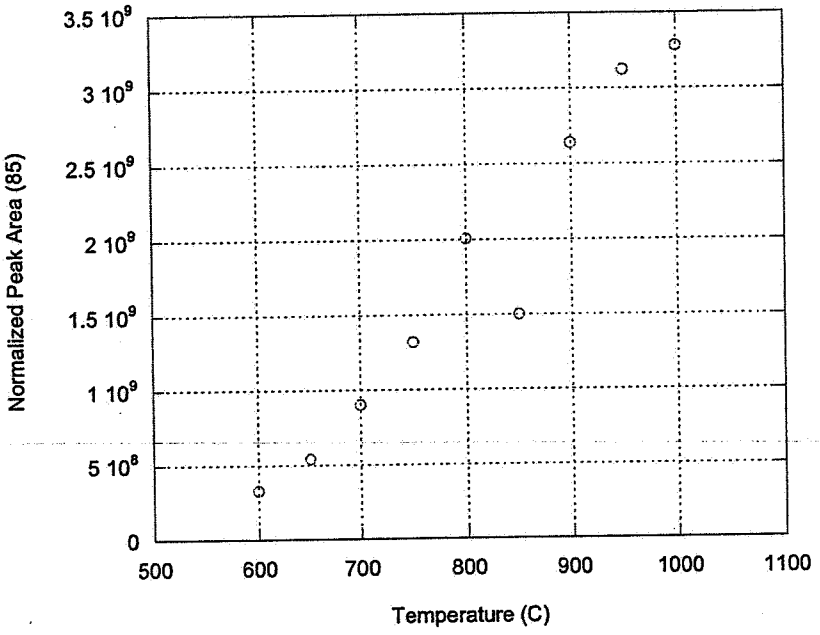


Figure 3.25 Temperature vs. Integrated Normalized Peak Area of Ion 85 (SiF_3).

3.4 Treated Article Gasification: XPS Analysis of Pyroprobe Cartridge

The surface of the sample cartridge used for treated article gasification was analyzed by XPS to determine if there was fluorine on the sample cartridge surface after pyrolysis. Table 3.6 shows the relative percentage of atom surface composition obtained from XPS analysis for one blank cartridge and one sample cartridge. The sample (1.15 mg) was gasified with synthetic air specifically for this study using the same pyroprobe and procedure applied for the combustion tests. Only C, O, and Si were detected showing evidence of C=O, C-O, C-C, and C-H bonding. The location of fluorine in the XPS results is shown in Figures 3.26, 3.27 and 3.28. No fluorine (F) peak is evident in either spectrum.. The relative carbon composition increased while O and Si compositions decreased for the cartridge used for sample gasification due to deposition of organic compounds on the cartridge surface during sample gasification.

Table 3.6 Approximate Atom % Surface Compositions.

Sample	C			O	Si
	C=O	C-O	C-C, C-H		
Blank	1.6	1.9	11.2	60.7	24.6
*Treated 1st	4.8	9.1	40.5	33.9	11.8
*Treated 2nd	5.2	9.5	55.0	23.1	7.2

* Sample cartridge for the treated article was analyzed twice.

Figures 3.26, 3.27, and 2.28 show XPS results for the blank cartridge, the first analysis of the sample cartridge, and the second analysis of the same cartridge, respectively.

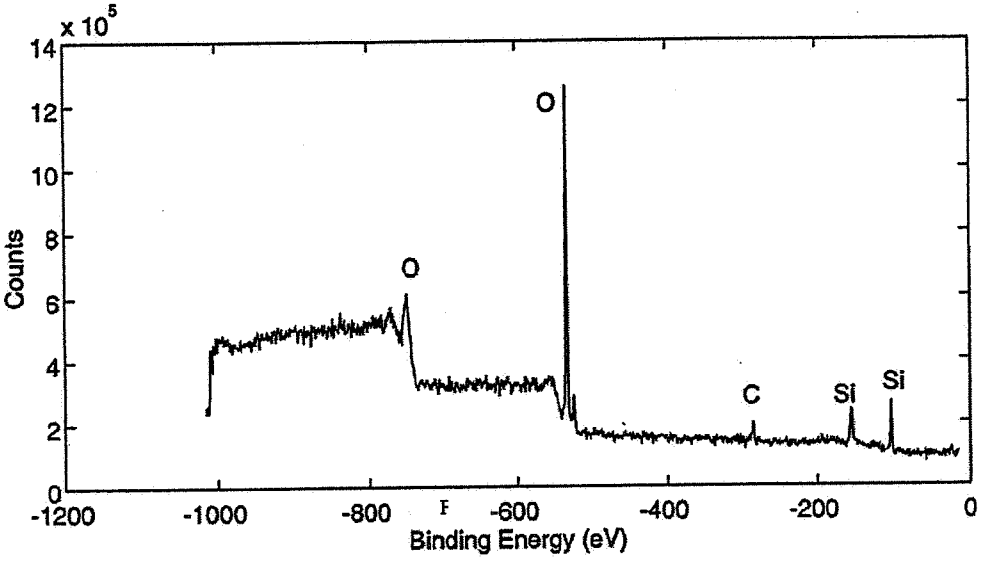


Figure 3.26 XPS Result for Blank Cartridge.

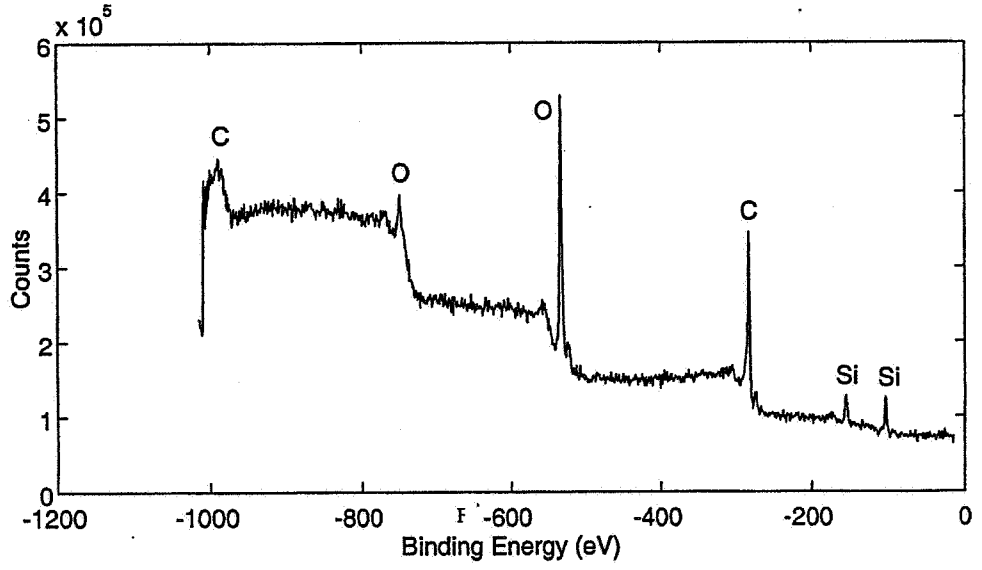


Figure 3.27 XPS Spectrum for Sample Cartridge (First Analysis).

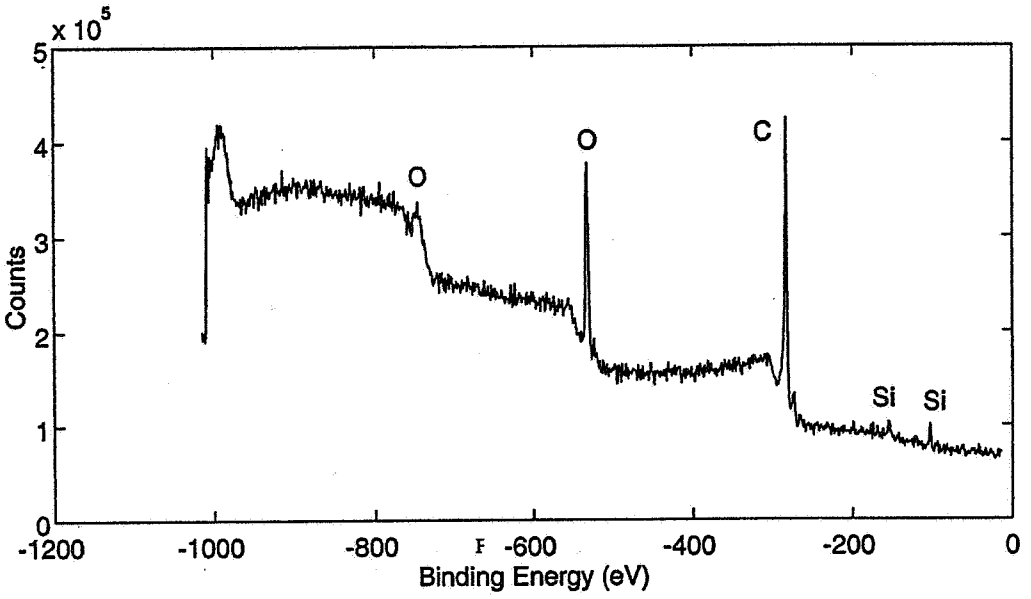


Figure 3.28 XPS Spectrum for Sample Cartridge (Second Analysis).

3.5 Telomer B Alcohol Combustion GC/MS Analysis

In-line GC/MS analysis was conducted for Telomer B Alcohol thermal decomposition at 200 and 600°C in order to confirm that ion 77 formation observed in the fluorinated acrylic polymer combustion tests was from decomposition of the "Telomer" ($X\text{-}CH_2CH_2\text{-}C_nF_{2n+1}$) functionality. Figure 3.29 shows extracted ion 77 ($\bullet CF_2CH{=}CH_2$) for Telomer B Alcohol thermal decomposition at 200 and 600°C. The mass of sample gasified and the integrated peak area for ion 77 ($\bullet CF_2CH{=}CH_2$) normalized by mass is presented in Table 3.7. The data suggests that compounds containing the $\bullet CF_2CH{=}CH_2$ fragment form in greater amounts with increasing temperature. Raw Data are provided in Appendix C.

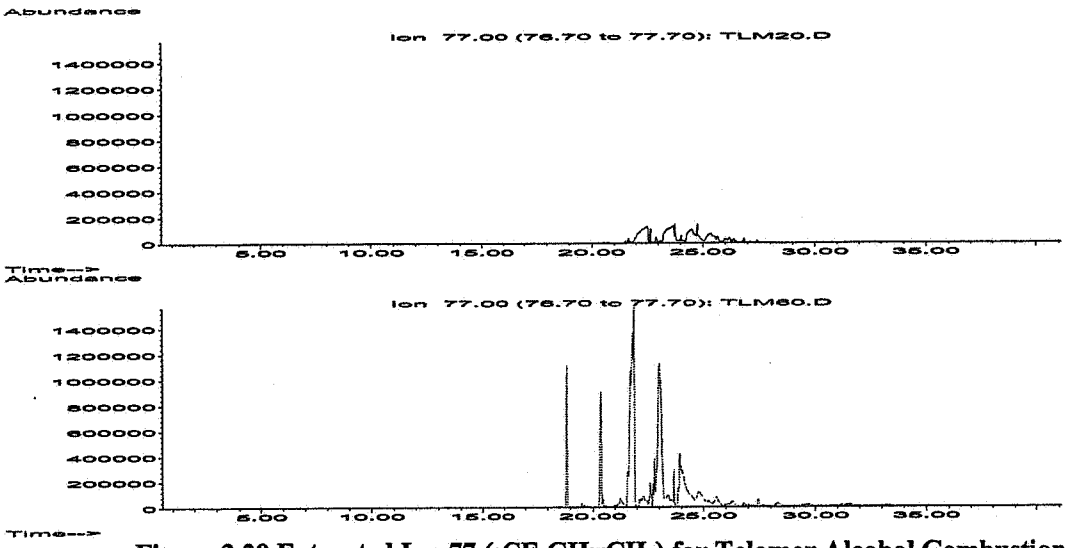


Figure 3.29 Extracted Ion 77 ($\bullet CF_2CH=CH_2$) for Telomer Alcohol Combustion at 200 and 600°C.

Table 3.7 Sample Gasified and Normalized Integrated Peak Area of Ion 77 ($\bullet CF_2CH=CH_2$).

Temperature (°C)	Gasified Mass (mg)	Normalized Peak Area
200	1.24	104114725
600	1.68	347271963

3.6 Treated & Untreated Articles: Off-line GC/MS VOC Analysis at 1000°C

VOCs from untreated and treated article combustion at 1000°C were collected in a Tedlar® bag and analyzed using off-line GC/MS analysis. Figures 3.30 and 3.31 show the total ion chromatogram of untreated and treated article combustion at 1000°C, respectively. Table 3.8 shows the net amount of sample gasified. All six chromatograms are nearly identical. Three major peaks in each chromatogram correspond to air, CO_2, and water. No other significant peaks were observed for both untreated and treated articles, indicating that volatile fluorocarbons were not detected.

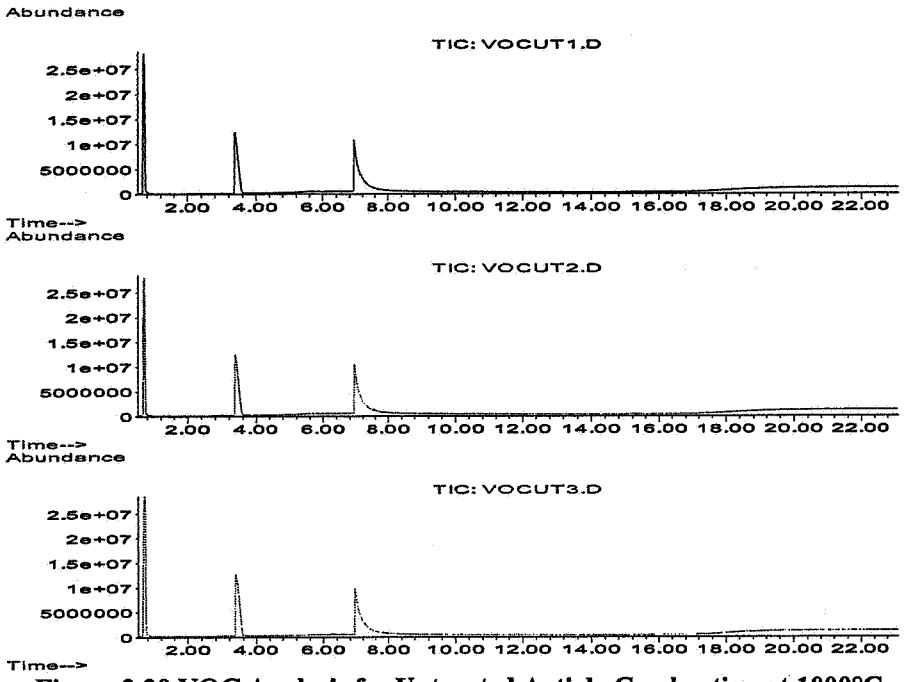


Figure 3.30 VOC Analysis for Untreated Article Combustion at 1000°C.

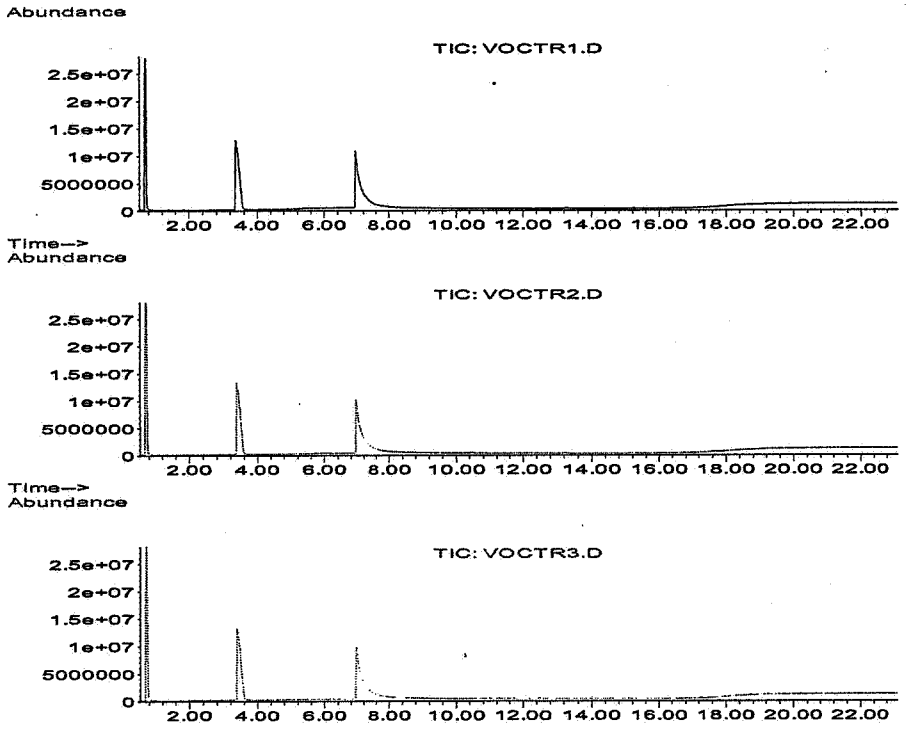


Figure 3.31 VOC Analysis for Treated Article Combustion at 1000°C.

Table 3.8 Net Mass of Sample Gasified.

Sample	Gasified Mass (mg)
Treated Article 1	2.18
Treated Article 2	2.24
Treated Article 3	2.09

3.7 Treated & Untreated Articles: CO and CO_2 Analyses at 1000°C

CO and CO_2 analyses from the combustion of the treated and untreated articles at 1000°C were conducted using off-line GC/TCD analysis. Table 3.9 shows the flow rate monitored, which is used to calculate gas exhaust volume (mL) and the number of moles of CO and CO_2 collected. Table 3.10 shows the concentration of CO and CO_2, number of moles of CO and CO_2 collected, number of mole gasified, and carbon recovery. Columns 2 and 3 in Table 3.10 show CO and CO_2 concentrations in the sampling bag, which are normalized by the mass of gasified samples. The average CO_2 concentration is almost identical for untreated and treated article combustion. The average CO concentration differs somewhat between untreated and treated article combustion. Columns 4 through 6 in Table 3.9 show the molar number of collected CO, CO_2 and their summation, respectively. Column 7 in Table 3.9 shows the molar number of gasified carbon calculated by sample weight and the relative carbon weight ratio provided by DuPont. Column 8 of Table 3.9 shows the carbon recovery, which is calculated based on the molar number of carbon collected and carbon gasified. Raw data for the VOC, CO and CO_2 analyses are provided in Appendix D.

Nearly 100% carbon recovery was obtained for both untreated and treated articles. The slight overestimation of the carbon recovery may result from the estimation of gas exhaust volume based on inlet flow rates before the sampling and collection time.

Table 3.9 Flow Rate Monitored for CO and CO_2 Analysis (Base Information Used for CO and CO_2 Recovery in Table 3.10).

Unit	Flow Rate				Gasification Time (sec)	Total Time (min)	Total Volume (mL)
	Inlet 1 (mL/min)	Inlet 2 (mL/min)	Makeup Gas (mL/min)	Total (mL/min)			
Untreated 1	6.8	8.7	4.2	19.7	53.39	4.89	96.33
Untreated 2	6.8	8.6	4.4	19.8	54.86	4.91	97.30
Untreated 3	6.8	8.7	4.3	19.8	51.18	4.85	96.09
Treated 1	6.8	8.8	4.4	20.0	68.10	5.14	102.70
Treated 2	6.7	8.8	4.5	20.0	66.87	5.11	102.29
Treated 3	6.8	8.9	4.5	20.2	62.20	5.04	101.74

Table 3.10 Carbon Recovery for Untreated and Treated Article Combustion at 1000°C.

Sample	Normalized CO Conc. (ppm)	Normalized CO_2 Conc. (ppm)	Total Gas Volume (mL)	CO Collected (Mol)	CO_2 Collected (Mol)	Number of C Collected (Mol)	Number of C Gasified (Mol)	Carbon Recovery (%)
Untreated 1	826	9712	96.33	7.09E-06	8.34E-05	9.05E-05	8.92E-05	101.4
Untreated 2	635	10165	97.30	5.66E-06	9.06E-05	9.62E-05	9.16E-05	105.0
Untreated 3	468	9756	96.09	3.85E-06	8.01E-05	8.39E-05	8.55E-05	98.2
Average	**643**	**9878**		**5.53E-06**	**8.47E-05**	**9.02E-05**	**8.88E-05**	**101.5**
Treated 1	351	9737	102.70	4.08E-06	1.13E-04	1.17E-04	1.15E-04	102.2
Treated 2	448	9485	102.29	5.09E-06	1.08E-04	1.13E-04	1.13E-04	100.2
Treated 3	321	10326	101.74	3.38E-06	1.09E-04	1.12E-04	1.05E-04	106.8
Average	**373**	**9849**		**4.18E-06**	**1.10E-04**	**1.14E-04**	**1.11E-04**	**103.1**

3.8. PFOA Absorption Study

3.8.1 PFOA in Aqueous Solution

The PFOA absorption and transport efficiency tests are summarized in Table 3.11 and 3.12.

The absorption tests showed that PFOA recovery fluctuated between 100 to 280%. The PFOA HPLC/MS/MS analysis measurement required multiple dilutions for the sample to be within the calibration range of the instrument. In the course of these analyses, the dilutions may not have been correctly recorded and thereby would account for the observed fluctuation in recoveries.

Table 3.11 Summary of PFOA Absorption Tests.

Test	PFOA Gasified (mg)	Water Volume			PFOA Concentration			Total PFOA (ng/L)	Recovered PFOA (mg)	PFOA Recovery (%)
		Jar 1 (mL)	Jar 2 (mL)	Jar 3 (mL)	Jar 1 (ng/L)	Jar 2 (ng/L)	Jar 3 (ng/L)			
Absorption 1	1.93	60	60	60	7970000	1000	17700000	25671000	4.62	239.4
Absorption 2	1.95	60	60	60	346000	2480	10500000	10848480	1.95	100.1
Absorption 3	1.96	60	60	60	3640	14100000	16900000	31003640	5.58	284.7

Due to the poor PFOA recovery results, Wickbold Torch analysis was conducted to evaluate PFOA recovery based on total fluorine. The experimental setup and methods are described in Appendix E and G, respectively. The results are shown in Table 3.12. The sample collected during the first absorption test (corresponding to Absorption 1 in Table 3.11) was analyzed. The results show 69.3% fluorine recovery. However, nearly 50% of the PFOA loaded was recovered in Jar 3, the rinseate from extraction of the absorption test apparatus. This indicates that significant PFOA condensation upstream of the sampling system occurred under the conditions of these tests. The protocol used for this study is described in Section 2.11.

Table 3.12 PFOA Recovery as Fluorine (Wickbold Torch Analysis). [Sample Used: Absorption 1]

Sample	Sample Weight (1) (g)	Water Volume (2) (mL)	Fluorine Weight (3) (µg)	Total Fluorine (3) × [(2)÷(1)] (mg)
Jar 1	2.9928	60	19.4	0.39
Jar 2	3.0200	60	1.2	0.02
Jar 3	2.9904	60	46.1	0.92
			Total (mg)	1.34
			Gasified (mg)	1.93
			Recovery (%)	69.3

3.9 PFOA Transport Studies

3.9.1 PFOA Transport Study - Aqueous Sampling

The transport efficiency test at 170°C showed very poor recoveries and large fluctuations from 0.5 to 4.4%. The transport efficiency test at 300°C showed improved yet still poor recoveries and smaller fluctuation (14.8 to 20.6%). The protocol used is described in Section 2.11.

Table 3.13 Summary of PFOA Transport Studies.

Test	PFOA Gasified (mg)	Water Volume		PFOA Concentration		Total PFOA (ng/L)	Recovered PFOA (mg)	PFOA Recovery (%)
		Jar 1 (mL)	Jar 2 (mL)	Jar 1 (ng/L)	Jar 2 (ng/L)			
Transport @170°C 1	1.68	65	60	72400	0	72400	0.01	0.5
Transport @170°C 2	1.71	65	60	604000	0	604000	0.08	4.4
Transport @170°C 3	1.9	65	60	662000	74.4	662074	0.08	4.4
Transport @170°C Blank	0	65	60	965	304	1269	0.00	N.A.
Transport @300°C 1	1.75	65	60	2070000	994	2070994	0.26	14.8
Transport @300°C 2	1.81	65	60	2980000	954	2980954	0.37	20.6
Transport @300°C 3	1.75	65	60	2550000	20000	2570000	0.32	18.4
Transport @300°C Blank	0	65	60	212000	510	212510	0.03	N.A.

To further analyze these samples, two aqueous solution samples were analyzed for total fluorine using the Wickbold Torch method. The first sample was from the first jar from the second transport efficiency test at 170°C. The second sample was from the first jar from the third transport efficiency test at 300°C. The results are shown in Table 3.14. The fluorine recovery was determined to be 9.8% at 170°C and 45.9% at 300°C. The PFOA recovery as total fluorine shows better results than the direct PFOA measurement. However, the low recoveries coupled with evidence of PFOA condensation from the total fluorine analysis of samples obtained from the absorption tests strongly suggest PFOA condensation in the unheated silicone tube transport line.

Table 3.14 Wickbold Torch Determination of Total Fluorine.

Sample	PFOA Gasified (mg)	Weight ratio of F in PFOA	Calculated Fluorine Gasified (µg)	Total Fluorine in Jar (µg)	F (%) Recovery
First jar of second transport efficiency test at 170°C	1.71	0.688	1176.5	115.2	9.8
First jar of third transport efficiency test at 300°C	1.75	0.688	1204.0	552.9	45.9

Following the initial transport tests described above, steam was used to extract the ATRS system according to the protocol described in Section 2.11.1. 5 mL of water was introduced as steam for each extraction followed by 5mL of water to rinse the tubing which connected the ATRS to the water bubblers. The steam extraction was performed after the all PFOA transport efficiency tests shown in Table 3.13

were conducted. Table 3.15 shows the steam extraction results. Over 80% of the steam was recovered from the system, except for the third extraction. The total PFOA recovered from the steam extraction was only 0.178 mg. The majority of PFOA was extracted during the first steam extraction. In addition, the pyroprobe was rinsed with water and analyzed. A negligible amount of PFOA was recovered as shown in Table 3.16. The sum of all the steam extractions and pyroprobe water rinse accounts for less than 2% of the total amount of PFOA introduced into the ATRS test system in these tests.

Table 3.15 PFOA Recovered from Steam Extraction.

Steam Extraction	Collected Steam (mL)	Rinse Water (mL)	Total Amount (mL)	PFOA Conc. (ng/L)	PFOA Recovered (mg)
1st	4.068	5	9.068	19200000	0.174
2nd	4.135	5	9.135	217000	0.002
3rd	2.195	5	7.195	92100	0.001
4th	4.336	5	9.336	79200	0.001
5th	4.285	5	9.285	55600	0.000
Total					0.178

Table 3.16 PFOA Recovered from Pyroprobe Rinsing.

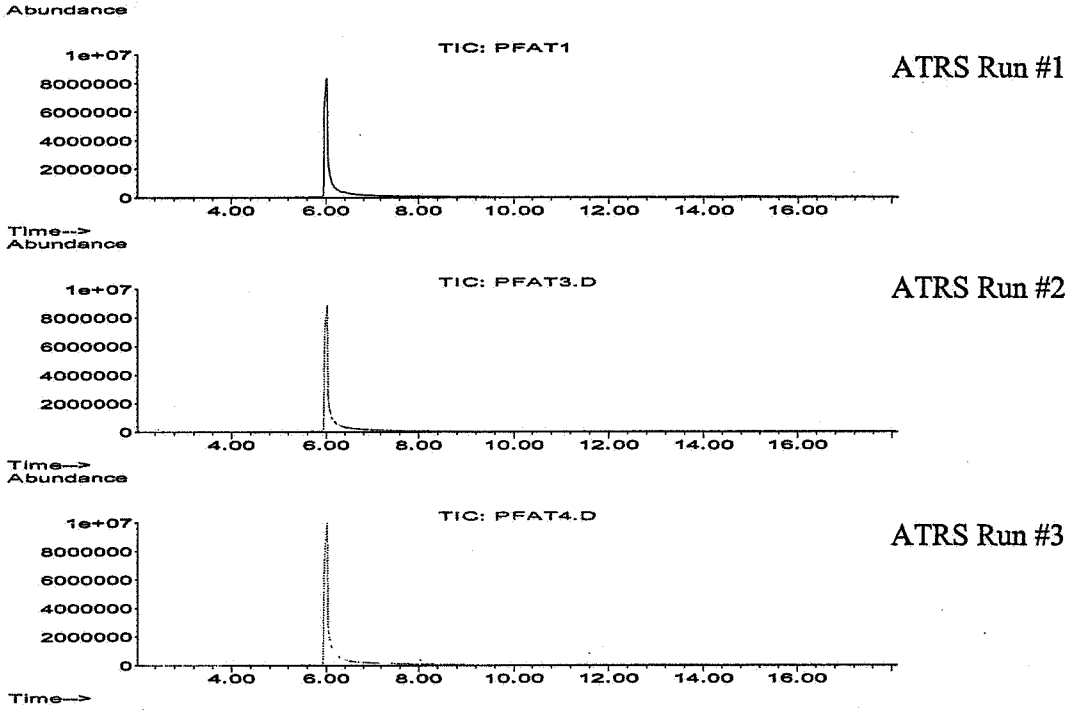
Pyroprobe Rinse	Water Used (mL)	PFOA Conc. (ng/L)	PFOA Recovered (μg)
1st	100	4295	0. 4
2nd	100	602	0. 1
3rd	100	0	0. 0
4th	100	0	0. 0
5th	100	0	0. 0
Total			0. 5

3.9.2 PFOA Transport Study - Gas Phase Sampling

The protocol for this test is described in Section 2.11.2. Table 3.17 shows integrated total ion peak area corresponding to PFOA. The first three areas were obtained from PFOA transported through the ATRS and the last three were obtained from direct injection of PFOA into the GC injection port. Two system blank runs were performed for the PFOA transport through the ATRS to confirm no sample carryover from the previous experiment. The first blank runs showed small amount of carryover and second blank runs show no carryover for all 3 samples. One system blank was performed for the direct injection of PFOA into the GC injection port and no carryover was identified from the blank run. The peak areas obtained from the blank runs were added to the peak area obtained from the first GC run as shown in Table 3.17. Each peak area was normalized by the gasified sample mass and the three determinations were averaged. Based on the average peak area, 74.3% of transport efficiency was obtained by taking the ratio of the Average Peak Area 1 over Average Peak Area 2. 74.3% is within generally accepted recovery criteria (70-130%, US EPA, 1996). Figures 3.32 and 3.33 show the total ion chromatogram for the PFOA transport through ATRS and GC injection port, respectively.

Table 3.17 PFOA Peak Area.

	Peak Area from First GC Run (1)	Peak Area from Blank Run (2)	Total Peak Area = (1) + (2)	Sample Mass (mg) (3)	Total Peak Area Normalized by Mass = [(1+2) ÷ 3]
ATRS Run #1	684994647	10510992	695505639	0.44	1580694634
ATRS Run #2	673277175	4069277	677346452	0.45	1505214338
ATRS Run #3	814730308	289003	815019311	0.45	1811154024
				Average Peak Area 1	1632354332
Direct GC 1	966189956	0	966189956	0.45	2147088791
Direct GC 2	1030933423	0	1.031E+09	0.48	2147777965
Direct GC 3	1033245273	0	1.033E+09	0.45	2296100607
				Average Peak Area 2	2196989121
			Transport Efficiency (%) (Peak Area 1) ÷ (Peak Area 2) × 100		74.3

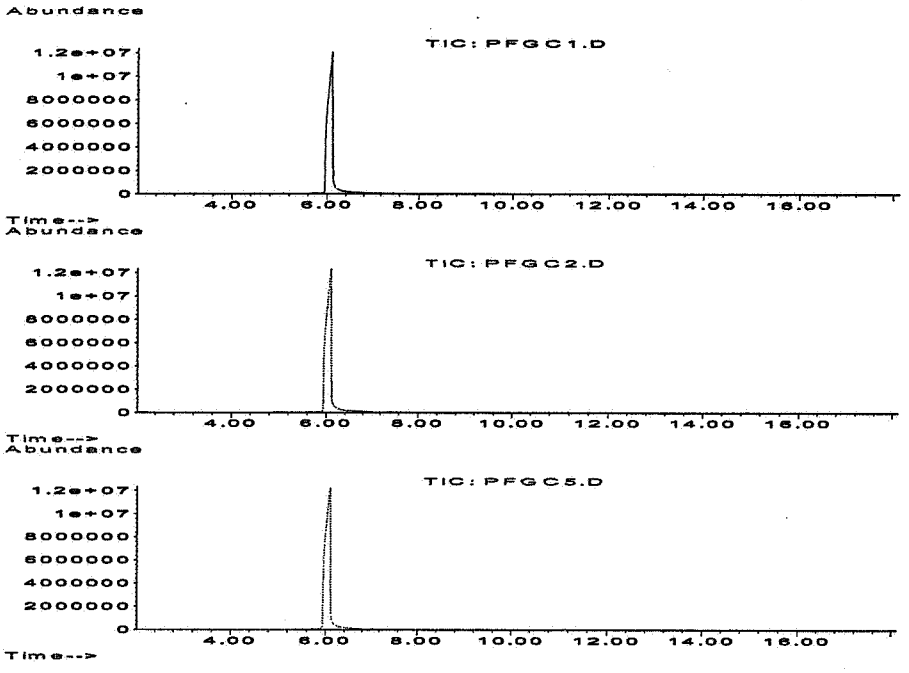


ATRS Run #1

ATRS Run #2

ATRS Run #3

Figure 3.32. Total Ion Chromatograms Obtained from PFOA Transport Test Through ATRS.



Direct GC 1

Direct GC 2

Direct GC 3

Figure 3.33. Total Ion Chromatograms Obtained from Direct Injection.

3.10 PFOA Calibration Curve and Detection Limit Studies

The mass of sample introduced and the corresponding peak area are tabulated in Table 3.18 and the calibration curve is shown in Figure 3.34. The extracted ion 131, which is the most abundant ion of the major PFOA ions, is shown in Figure 3.35 for 1.10, 5.50, 10.16, 50.80, and 100.40 μg injection. PFOA appeared at a 16 min retention time. A secondary peak emerged for 50.80 and 100.40 μg injection; however, the mass spectrum shows a nearly identical pattern for the main and secondary peaks as shown in Figure 3.38. Both peaks were integrated and summed to determine the peak area. The secondary peaks at varying retention times may be attributed to the sorption and desorption in the detector due to the relatively large quantity and the high polarity of the analyte. Raw data for this study is presented in Appendix F.

Table 3.18 PFOA Mass vs. Corresponding Peak Area.

PFOA	Ion 131 Peak Area		
Mass (μg)	1st	2nd	Average
1.10	293383	456475	374929
5.50	2554771	2893790	2724281
10.16	5692993	5769835	5731414
50.80	28143180	23799422	25971301
100.40	50366258	45606352	47986305

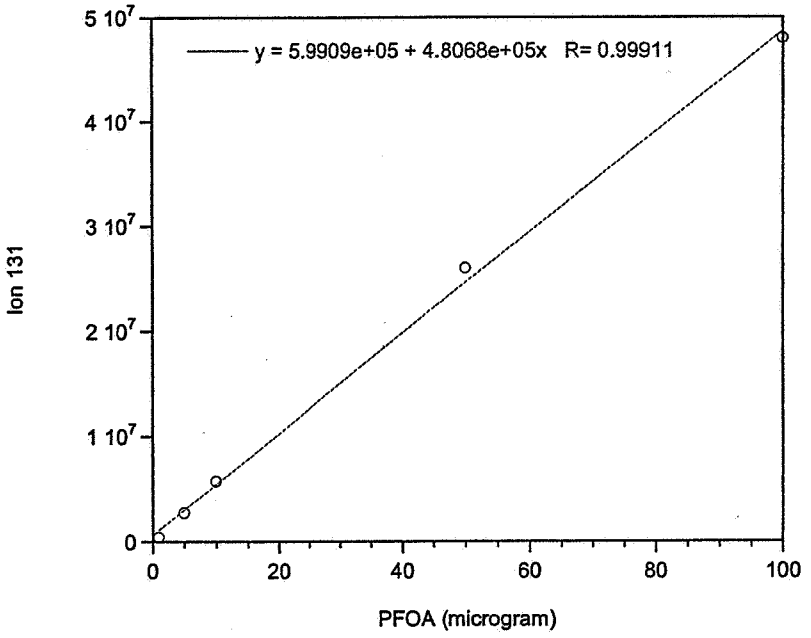


Figure 3.34. PFOA Calibration Curve.

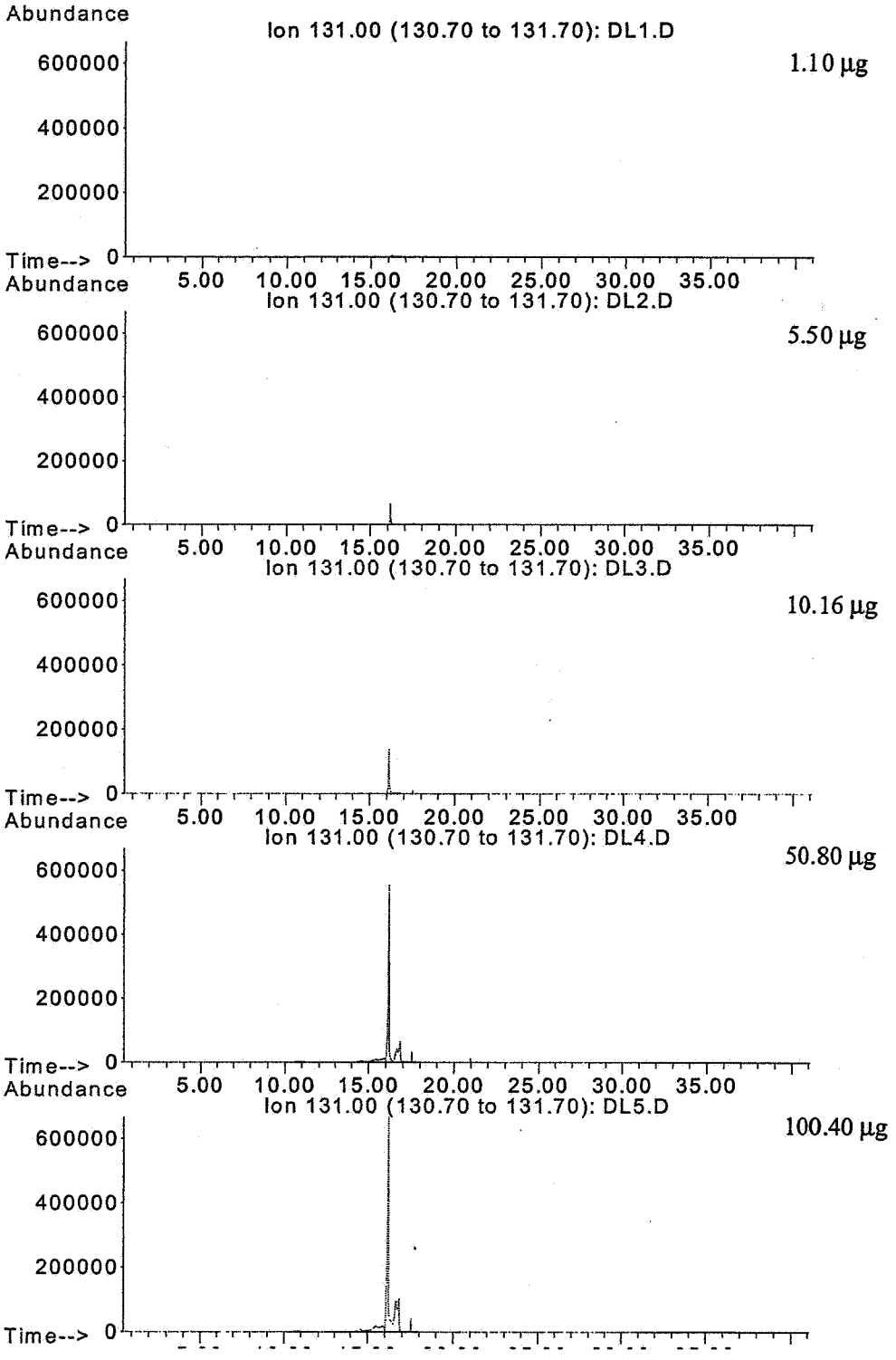


Figure 3.35. PFOA Extracted Ion (131) Chromatograms for 1.10, 5.50, 10.16, 50.80, and 100.40 µg.

Figure 3.36 shows the reference spectrum of PFOA obtained from the NIST129K library (G1701BA Version B03.00, Agilent Technologies). The five most abundant ions shown in the reference spectra are 131 ($\bullet CF_2CF{=}CF_2$), 69 ($\bullet CF_3$), 31 (CF), 44 (CO_2), and 93 (C_3F_3), in this order.

Figure 3.37 shows the full scan PFOA peak spectra for the 100.40, 50.80, 10.16, 5.50, and 1.10 µg injections. The spectra contained ions 131, 69, 31, and 93. These common ions were used to establish the PFOA detection limit. All of the PFOA peak spectra, from 100.40 to 1.10 µg, show major ions with similar abundance ratio to the reference spectra. However, the spectra for the 1.10 µg injection shows ion 18 as the third largest ion, which is not compatible with the reference spectra. Ion 18 is water, H_2O, associated with background trace water in the test system. The PFOA limit of quantitation (LOQ) was established using extracted ion 131and is 1 µg based upon 1 µg as the lowest standard of calibration. The limit of detection (LOD) is lower than the LOQ. PFOA full scan spectrum for 1.10 µg injection shows that the signal (131) to noise (S/N) ratio is more than 20. Therefore, LOD could be less than one sixth (1/6.67) of LOQ if S/N of LOD is defined as ca. 3:1.

Based on the 1.10 µg limit of quantitation (LOQ), on a mass basis obtained in this study, the detection limit of gas phase PFOA concentration can be estimated. Typical gasification times were 20 to 30 sec for the articles and 30 to 40 sec for the polymer combustion tests. The gasification time of 30 sec provides 0.94 mL/sec × 30 sec = 28.20 mL synthetic air at 25°C. The molar amount of 1.10 µg PFOA is 1.10×10^{-6} / 414 = 2.66×10^{-9} mol, which gives gas phase volume of:

$[2.66\times10^{-9}(mol)\times0.0821(atm\text{-}l/mol\text{-}K)\times298K]/1atm\times1000mL/l = 65.1\times10^{-6}$ mL at 25°C.

1 µg PFOA can produce gas phase concentration of $59.2\times10^{-6}/28.2 = 2.31$ ppm by volume. Therefore, the gas-phase LOQ and LOD are 2.31 and ca.. 0.35 ppm, respectively.

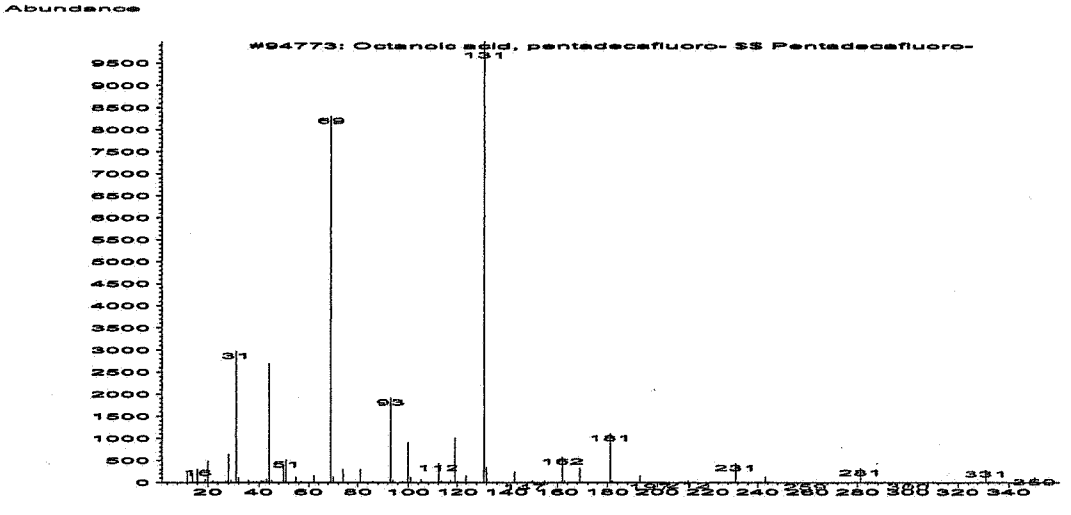


Figure 3.36. PFOA Reference Spectra Obtained from NIST129K Library.

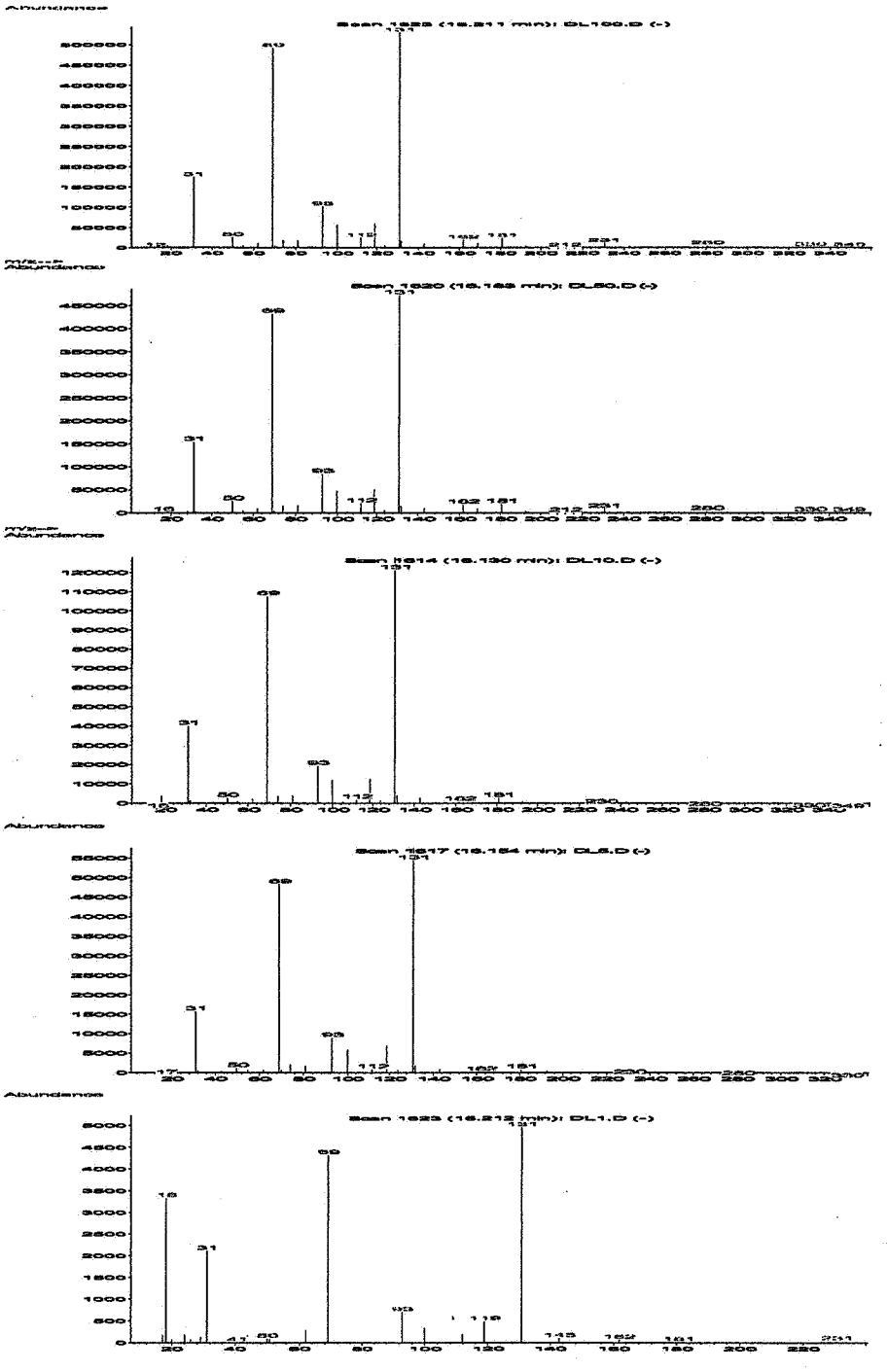


Figure 3.37. PFOA Full Scan Spectra for 100.40, 50.80, 10.16, 5.50, and 1.10 µg Injection.

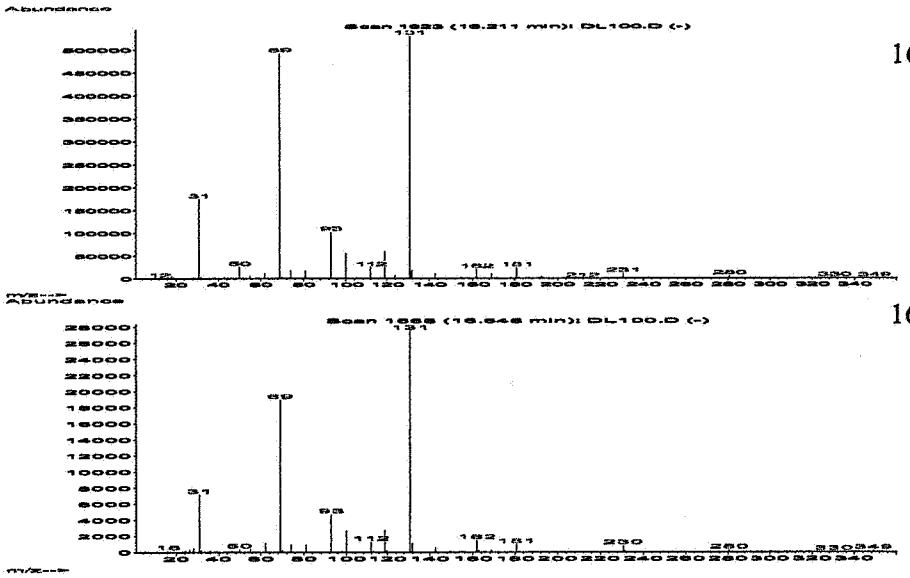


Figure 3.38. PFOA Full Scan Peak Spectra at 16.2 and 16.6 min for 100 µg Injection.

3.11 PFOA Analysis from Combustion Tests of the Treated & Untreated Articles and the Fluorinated Acrylic Polymer Using In-line GC/MS Analysis

The ion chromatograms obtained from the actual treated and untreated article combustion tests shown in Section 3.1 were examined to identify the potential existence and quantity of PFOA. Ion 131 was selected for this analysis because it was the largest based on the calibration work in Section 3.9 and the standard reference library spectrum. Figures 3.39 and 3.40 show extracted ion 131 chromatograms for the treated and untreated article combustion tests at 600, 650, 700, 725, and 1000°C. The elution time between 14 and 18 min was monitored because this is where PFOA is expected to elute under these GC conditions. No PFOA peak was detected at a limit of detection of 0.35 ppm. Figures 3.41 and 3.42 show extracted ion 131 chromatograms for the fluorinated acrylic polymer at 600 to 800°C and 850 to 1000°C. Peaks appear at 16.35, 17.10, 17.70 and 17.95 min at temperatures of 600, 650, 700, and 750°C. None of these peaks are for PFOA based upon evaluation of their mass spectra which are shown in Figure 3.43. The peak at 16.35 min is tentatively identified as C_6HF_{13}, based on the NIST library. None of the other peaks correlated with a reference spectrum in the NIST library.

The re-examination of the ion chromatogram for the actual combustion tests shows that there is no indication of PFOA formation at the sub-ppm level for the three samples studied at the temperature between 600 to 1000°C with 85% excess air.

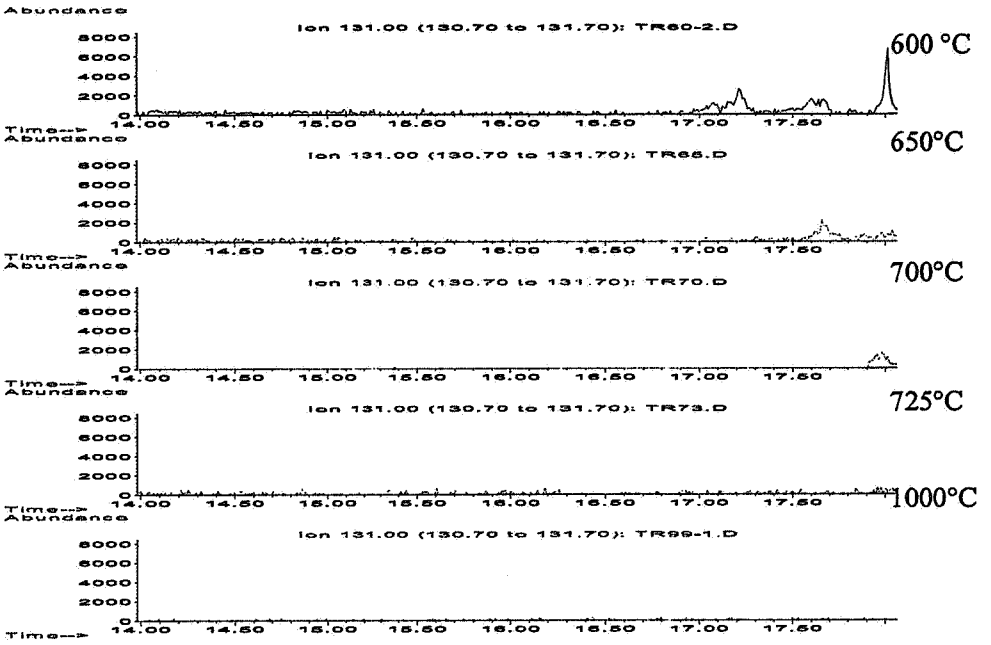


Figure 3.39. Extracted Ion 131 for Treated Article from 14 to 18 min Retention Time at 600, 650, 700, 725, and 1000°C.

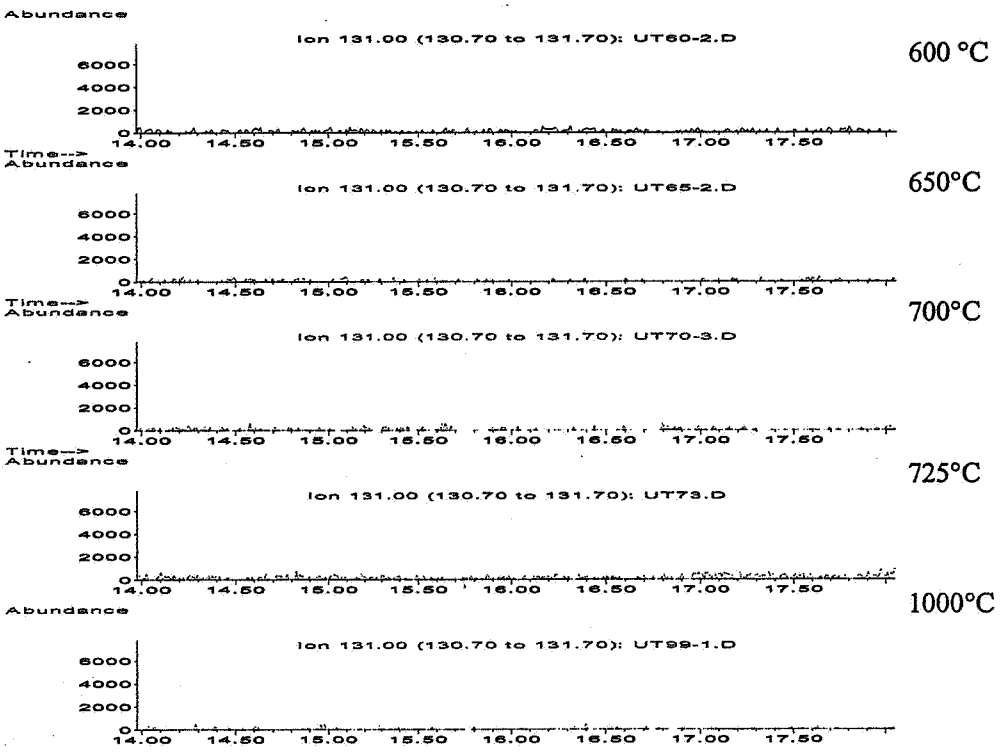


Figure 3.40. Extracted Ion 131 for Untreated Article from 14 to 18 min Retention Time at 600, 650, 700, 725, and 1000°C.

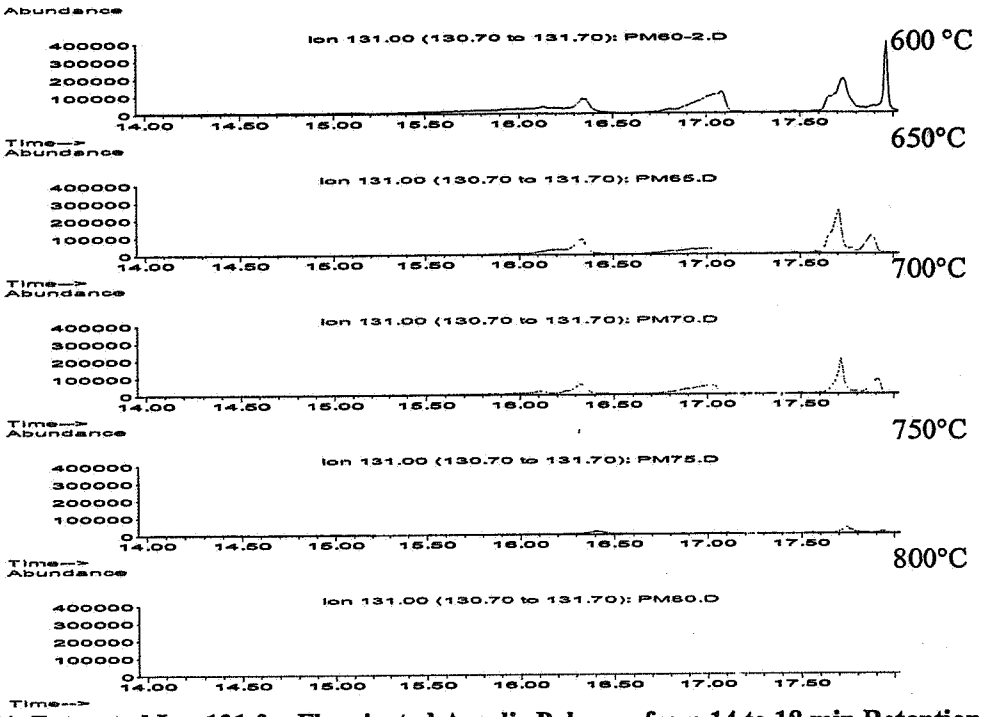


Figure 3.41. Extracted Ion 131 for Fluorinated Acrylic Polymer from 14 to 18 min Retention Time at 600, 650, 700, 750, and 800°C.

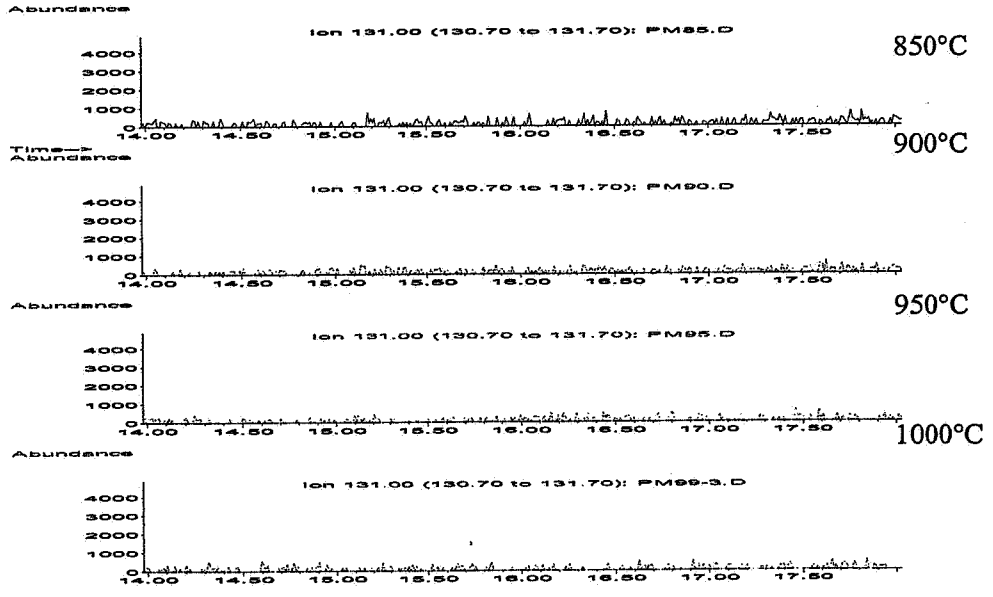


Figure 3.42. Extracted Ion 131 for Fluorinated Acrylic Polymer from 14 to 18 min Retention Time at 850, 900, 950, and 1000°C.

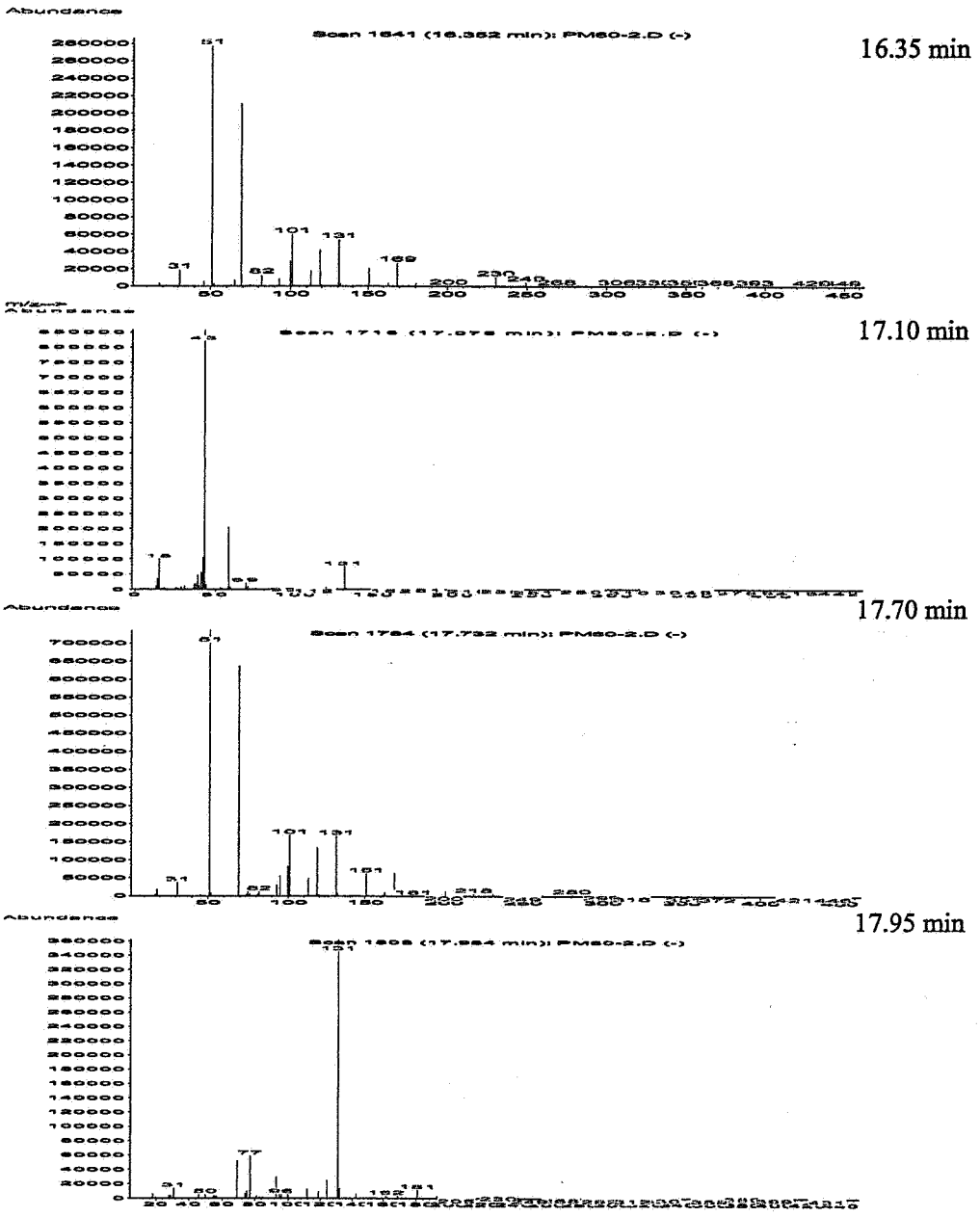


Figure 3.43. Spectra for the Peaks at 16.35, 17.10, 17.70, and 17.95 min at 600°C in Figure 3.41.

4. Discussion

The purpose of this study was to investigate the thermal degradation of a polyester/cellulose fabric substrate ("article") treated with fluorotelomer-based acrylic polymer under laboratory conditions conservatively representing typical municipal waste combustor conditions of time, temperature, and excess air level. The treated article is reasonably expected to be present in municipal waste as discarded textile or paper. Therefore, the principal focus of this work was to determine the environmental fate of the treated article when it is incinerated. Supplementary studies examined an untreated article, the fluorotelomer-based acrylic polymer, and Telomer B Alcohol raw material to assist in the interpretation of the experimental observations for the treated article.

The test protocols used were similar to those developed for recent testing of fluorinated materials (Yamada and Taylor, 2003, Graham, 2002). Thermogravimetric analysis was used to define the gasification conditions. Thermal experiments were then conducted at non-flame reactor temperatures from 600 to 1000°C for a mean, gas-phase residence time of 2.0 sec. 85% excess air was used for all experiments. The studies emulated typical municipal waste incinerator combustion conditions with an average temperature of 1000°C or greater over approximately 2 sec residence time (Giraud, 2004).

Combustion tests for the treated article, the untreated article, and the fluorotelomer-based acrylic polymer were completed. The following objectives were addressed: 1) determination of the temperature for 99.9% conversion, 2) determination of major products of incomplete combustion at 1000°C for the treated and untreated article, 3) determination of carbon mass balances at 1000°C for the treated and untreated article, 4) determination of the concentration of PFOA in the effluent from all tests, and 5) determination of the concentration of fluoride ion in the 1000°C tests for the treated and untreated articles.

The temperature for 99.9% destruction of the treated and untreated articles was 725°C. This temperature regime (700-750°C) for 99.9% conversion is consistent with the results of prior tests of hydrocarbon-based materials using UDRI thermal instrumentation systems (Dellinger, et al. 1984; Dellinger, 1989; Taylor, et al. 1990). The temperature for 99.9% destruction ($T_{99.9}$) of the fluorotelomer-based acrylic polymer was 1000°C. The $T_{99.9}$ value for the fluorotelomer-based acrylic polymer was slightly higher than that measured for other fluorinated materials using the same experimental apparatus (Graham, 2002). The difference may be related to the levels of excess air present in the respective combustion tests. Combustion tests with the fluorotelomer-based acrylic polymer used 85% excess air, while previous tests with other fluorinated materials employed considerably higher excess air levels.

Excellent carbon mass balances were obtained from the combustion tests of the untreated and treated articles (101.9 and 103.6%, respectively) at 1000°C. The only product of incomplete combustion that was observed under these conditions was carbon monoxide. Fluorinated organic byproducts were not observed via GC/MS in the combustion tests of the treated and untreated articles. In-line GC/MS was employed to determine the presence of heavier, less volatile fluorinated byproducts. None were identified. Additionally, off-line GC/MS was employed to determine the presence of volatile fluorinated byproducts in the gas exhaust from the 1000°C tests of the treated and untreated articles. None were identified.

Combustion tests of the fluorotelomer-based acrylic polymer were conducted to facilitate interpretation of the treated article combustion results. At 1000°C, 99.9% destruction of the polymer was observed. Based upon this result, the fluorotelomer-based acrylic polymer would be destroyed under typical municipal incinerator conditions. Analysis of the reactor effluent from additional combustion tests of the fluorotelomer-based acrylic polymer indicated the formation of a variety of compounds at temperatures

below 1000°C. Many of these compounds could not be identified using either the NIST mass spectral library or manual mass spectral interpretation. As a result, a limited number of combustion experiments were conducted on the Telomer B Alcohol raw material to try to determine the origin of these unidentifiable peaks. The experiments confirmed that selected ions were the same for the polymer and alcohol indicating their origin was indeed from the telomer functionality. Potential volatile combustion byproducts from the combustion of the fluorotelomer-based acrylic polymer were not analyzed.

Of additional interest was to determine whether PFOA was formed as a result of combustion of the treated article to determine if incineration of treated articles may be a source of PFOA in the environment. Analysis for PFOA in combustion tests of the treated and untreated article at 1000°C using both HPLC/MS/MS and in-line GC/MS were conducted. No detectable level of PFOA was determined. It can therefore be concluded that under typical municipal waste incineration conditions no significant quantity of PFOA would be formed from the incineration of a textile or paper substrate treated with a fluorotelomer-based acrylic polymer.

In addition, transport efficiency tests for PFOA using aqueous sampling (followed by HPLC/MS/MS results) and gas-phase sampling (followed by in-line GC/MS analysis) were conducted. Aqueous sampling with HPLC/MS/MS analysis produced transport efficiencies of less than 20% using ATRS reactor and transfer line temperatures of 170°C. Alternatively, in-line GC/MS tests using ATRS reactor and transfer line temperatures of 235°C produced transport efficiencies of greater than 70% (determined by dividing the ATRS PFOA response by the response obtained by direct injection of PFOA into the gas chromatograph). A plausible PFOA loss mechanism during the aqueous sampling transport tests may have involved absorption onto the unheated silicone transfer line tubing between the ATRS vent and the bubblers (see Fig. 2.15). The basis for this hypothesis was the strong interaction observed between PFOA and the DB-5 capillary column support (phenyl-methyl siloxane) during the in-line GC/MS analysis and the evidence for PFOA condensation in the absorption and transport tests. Cryogenic temperatures were not required to trap PFOA. PFOA was effectively trapped using this column at a temperature of 40°C, thus indicating a strong interaction between the capillary column support and the analyte of interest.

Based upon the combustion product analyses, it was clear that carbon-fluorine bonds were severed at 1000°C. This would result in the formation of fluorine atoms [F]. Fluorine atoms are highly reactive and would be expected to form hydrogen fluoride [HF] by reaction with hydrogen available in the combustion matrix. Analysis for fluoride ion (indicative of HF formation) in combustion tests of the treated and untreated article at 1000°C by trapping the gaseous effluent in aqueous bubblers followed by sampling and ion chromatography indicated fluoride [F^-] below analytical detection limits. Subsequent examination of different sections of the experimental apparatus provided clues as to what happened to the fluoride generated from combustion. XPS analysis of the pyroprobe cartridges used to contain the test sample did not indicate the presence of fluorine on the surface. Removal and visible examination of the high-temperature reactor did, however, indicate significant etching of the reactor surface, most notably downstream of the midpoint of the reactor. This is very likely due to the reaction of hydrogen fluoride (HF) with the silica groups (SiO_2, SiOH) of the reactor surface. Strong evidence confirming this interpretation was obtained from in-line GC/MS total ion chromatograms from the combustion of the fluorotelomer-based acrylic polymer at temperatures between 600 and 1000°C. Silicon tetrafluoride (SiF_4) was observed as a byproduct in these tests. The signal response for SiF_4 showed a near-linear increase with increasing temperature, consistent with increasing yields of HF at higher temperature arising from carbon-fluorine bond breaking. SiF_4 has been observed in previous combustion tests of highly fluorinated materials using high-temperature fused silica reactors (Yamada and Taylor, 2003, Graham, 2002). In the test system, carbon-fluorine bond breaking does occur. In summary, the fluoride formed from carbon-fluorine bond breaking reacts with the silica surface of the test apparatus to form silicon tetrafluoride.

5. Conclusions

This study reports the first known studies to investigate the thermal degradation of a polyester/cellulose fabric substrate ("article") treated with a fluorotelomer-based acrylic polymer under laboratory conditions conservatively representing typical municipal incineration conditions of time, temperature, and excess air level. The treated article is reasonably expected to be present in municipal waste as discarded textile or paper. Therefore, the principal focus of this work was to determine the environmental fate of the treated article when it is incinerated.

Laboratory-scale incineration studies of the treated article, untreated article and the fluorotelomer-based acrylic polymer were conducted. Combustion tests from 600-1000°C for gas-phase residence times of 2.0 sec and excess air levels of 85% indicated that 99.9% destruction was achieved at temperatures of 725°C (treated and untreated article) and 1000°C (fluorotelomer-based acrylic polymer). Analysis of the reactor effluent indicated that laboratory-scale incineration of these materials does not emit detectable levels of PFOA. Aqueous sampling (followed by off-line HPLC/MS/MS analysis) and in-line GC/MS analysis was used to analyze for PFOA. Transport efficiency testing indicated the in-line sampling to be the most accurate sampling method. The detection limit for PFOA analysis using in-line sampling followed by GC/MS analysis was 0.35 ppmv in the gas phase.

Excellent carbon mass balances were obtained from the incineration tests of the treated and untreated articles at 1000°C. Fluorinated combustion byproducts were not observed for combustion of these samples under these conditions. Attempts to recover fluorine from the combustion tests as HF were unsuccessful. Fluoride formed appears to have reacted rapidly with the silica surfaces of the test system. The detection of SiF_4 in the reactor effluent is a strong indication of the likelihood of this interaction.

These results demonstrate that the polyester/cellulose fabric treated with a fluorotelomer-based acrylic polymer is destroyed and no detectable amount of PFOA is formed under typical municipal incineration conditions. Therefore, textiles and paper treated with such a fluorotelomer-based acrylic polymer disposed of in municipal waste and incinerated are expected to be destroyed and not be a significant source of PFOA in the environment.

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Appendix A

Experimental Condition (Temperature, Flow Rate, and Pressure) and Total Ion Chromatograms for In-line GC/MS Analysis

Appendix A

LIST OF FIGURES

LIST OF TABLES

Table A1. Nominal Flow Rate at Different Temperatures

Temp (°C)	Inlet 1 (mL/min)	Inlet 2 (mL/min)
600	12.8	6.4
650	12.1	6.1
700	11.5	5.8
725	11.2	5.6
750	11.0	5.5
800	10.4	5.2
850	10.0	5.0
900	9.6	4.8
950	9.2	4.6
1000	8.8	4.4

Table A2. Experimental Condition of Untreated Article Combustion Test (Before and After)

Sample[a] (bef/aft)	Set T[b] °C	F. R. 1[c] mL/min	F. R. 2[d] mL/min	T 1[e] °C	T 2[e] °C	T 3[e] °C	T 4[e] °C	T 5[e] °C	T 6[e] °C	T 7[e] °C	Pres[f] atm
Blank (bef)	600	12.8	6.4	301	300	325	601	345	305	-125	A.P.
Blank (aft)	600	12.9	6.5	299	301	322	600	340	301	-130	A.P.
UT	600	12.9	6.4	300	301	309	601	328	300	-125	A.P.
UT	600	12.9	6.4	300	300	309	600	330	297	-130	A.P.
Blank	650	12.2	6.0	300	300	315	651	343	303	-125	A.P.
Blank	650	12.1	6.1	299	300	318	651	349	300	-127	A.P.
UT	650	12.1	6.1	299	300	324	650	353	312	-125	A.P.
UT	650	11.9	6.0	300	300	325	625	357	306	-130	A.P.
Blank	700	11.4	5.7	300	300	343	701	382	315	-125	A.P.
Blank	700	11.3	5.8	300	301	343	702	380	313	-130	A.P.
UT	700	11.5	5.7	300	300	345	702	384	314	-125	A.P.
UT	700	11.4	5.7	300	300	346	702	386	311	-128	A.P.
Blank	725	11.3	5.7	299	301	377	726	416	295	-125	A.P.
Blank	725	11.1	5.7	299	300	377	726	417	295	-128	A.P.
UT	725	11.3	5.6	299	301	375	725	413	297	-125	A.P.
UT	725	11.1	5.5	301	302	374	724	415	299	-127	A.P.
Blank	750	10.9	5.6	299	300	331	750	376	295	-125	A.P.
Blank	750	10.9	5.5	299	299	340	750	380	297	-125	A.P.
UT	750	10.9	5.5	300	300	366	750	414	313	-125	A.P.
UT	750	10.9	5.5	301	301	368	750	414	310	-129	A.P.
Blank	750	10.9	5.6	299	300	331	750	376	295	-125	A.P.
Blank	750	10.9	5.5	299	299	340	750	380	297	-125	A.P.
UT	750	11.1	5.6	300	299	347	750	388	297	-125	A.P.
UT	750	11.0	5.6	300	301	349	749	391	298	-128	A.P.
Blank	1000	8.9	4.4	300	301	496	1000	584	306	-125	A.P.
Blank	1000	8.6	4.2	299	301	507	1001	592	362	-127	A.P.
UT	1000	8.8	4.4	302	301	529	1000	611	406	-123	A.P.
UT	1000	8.9	4.4	301	301	532	1000	611	406	-123	A.P.

[a] Conditions were monitored and logged before and after the experiment. Blank: blank experiment before combustion, UT: untreated article

[b] Reactor set temperature

[c] Inlet 1 flow rate

[d] Inlet 2 flow rate

[e] Measured temperature at each position

[f] Reactor pressure, AP: atmospheric pressure

Table A3. Experimental Condition of Treated Article Combustion Test (Before and After)

Sample[a] (bef/aft)	Set T[b] °C	F. R. 1[c] mL/min	F. R. 2[d] mL/min	T 1[e] °C	T 2[e] °C	T 3[e] °C	T 4[e] °C	T 5[e] °C	T 6[e] °C	T 7[e] °C	Pres[f] atm
Blank (bef)	600	12.8	6.3	300	301	341	600	360	305	-125	A.P.
Blank (aft)	600	12.9	6.3	299	300	320	600	334	297	-130	A.P.
TR	600	12.8	6.3	299	299	313	599	327	298	-125	A.P.
TR	600	12.8	6.4	299	300	315	601	324	300	-125	A.P.
Blank	650	12.0	6.2	300	299	309	649	332	305	-125	A.P.
Blank	650	12.1	6.2	300	300	311	650	335	305	-128	A.P.
TR	650	12.0	6.2	300	301	312	650	335	311	-125	A.P.
TR	650	12.0	6.2	299	301	312	651	338	303	-123	A.P.
Blank	700	11.4	5.7	299	300	326	700	360	308	-125	A.P.
Blank	700	11.5	5.7	299	300	328	702	364	311	-128	A.P.
TR	700	11.4	5.9	299	301	333	701	365	319	-125	A.P.
TR	700	11.5	5.8	300	299	339	700	374	306	-128	A.P.
Blank	725	11.3	5.5	301	301	372	727	411	295	-125	A.P.
Blank	725	11.2	5.4	301	302	374	727	413	294	-126	A.P.
TR	725	11.2	5.5	300	302	373	725	410	298	-125	A.P.
TR	725	11.2	5.4	299	301	374	724	411	299	-123	A.P.
Blank	750	10.9	5.6	299	299	349	751	391	298	-125	A.P.
Blank	750	10.9	5.6	300	300	351	751	395	299	-130	A.P.
TR	750	11.0	5.6	300	299	354	750	396	299	-125	A.P.
TR	750	10.9	5.6	300	300	354	751	398	297	-128	A.P.
TR	750	11.0	5.5	300	300	356	750	398	299	-125	A.P.
TR	750	10.9	5.5	299	300	356	751	399	297	-125	A.P.
Blank	1000	8.9	404	302	300	532	1001	611	425	-125	A.P.
Blank	1000	8.9	4.5	299	299	533	1000	612	419	-125	A.P.
TR	1000	8.8	4.4	299	301	534	1002	612	430	-125	A.P.
TR	1000	8.9	4.5	299	300	535	1001	614	424	-127	A.P.

[a] Conditions were monitored and logged before and after the experiment. Blank: blank experiment before combustion, TR: treated article

[b] Reactor set temperature

[c] Inlet 1 flow rate

[d] Inlet 2 flow rate

[e] Measured temperature at each position

[f] Reactor pressure, AP: atmospheric pressure

Table A4. Experimental Condition of Fluorinated Acrylic Polymer Combustion Test (Before and After)

Sample[a] (bef/aft)	Set T[b] °C	F. R. 1[c] mL/min	F. R. 2[d] mL/min	T 1[e] °C	T 2[e] °C	T 3[e] °C	T 4[e] °C	T 5[e] °C	T 6[e] °C	T 7[e] °C	Pres[f] atm
Blank (bef)	600	12.8	6.5	250	250	304	602	334	305	-125	A.P.
Blank (aft)	600	12.7	6.4	251	250	299	600	327	312	-125	A.P.
PM	600	12.7	6.3	250	250	295	599	314	309	-125	A.P.
PM	600	12.9	6.3	250	250	293	599	313	306	-127	A.P.
Blank	650	12.1	6.1	251	251	295	651	328	295	-125	A.P.
Blank	650	12.0	6.1	249	249	294	650	329	297	-128	A.P.
PM	650	12.2	6.2	250	250	295	650	330	308	-125	A.P.
PM	650	12.1	601	250	250	295	650	330	301	-128	A.P.
Blank	700	11.5	5.7	249	251	307	700	357	307	-125	A.P.
Blank	700	11.6	5.8	250	250	310	702	357	303	-124	A.P.
PM	700	11.4	5.9	251	251	314	700	358	310	-125	A.P.
PM	700	11.5	5.8	249	251	314	701	360	309	-128	A.P.
Blank	750	11.0	5.4	249	250	318	750	374	312	-125	A.P.
Blank	750	10.9	5.4	249	251	323	750	379	311	-125	A.P.
PM	750	11.0	5.4	250	251	331	750	385	317	-125	A.P.
PM	750	10.9	5.4	249	251	332	748	387	303	-127	A.P.
Blank	800	10.4	5.2	251	250	356	801	416	310	-125	A.P.
Blank	800	10.6	5.1	251	252	357	800	420	307	-126	A.P.
PM	800	10.4	5.2	251	250	361	800	423	305	-125	A.P.
PM	800	10.4	5.1	250	251	362	800	424	310	-126	A.P.
Blank	850	10.0	5.0	251	250	361	849	436	296	-125	A.P.
Blank	850	10.0	5.0	251	251	369	850	444	296	-128	A.P.
PM	850	10.1	5.0	251	250	388	851	458	318	-125	A.P.
PM	850	10.1	5.0	249	250	390	850	462	315	-127	A.P.
Blank	900	9.7	4.7	250	250	411	900	491	321	-125	A.P.
Blank	900	9.6	4.7	250	252	414	899	492	326	-128	A.P.
PM	900	9.7	4.7	251	250	420	899	500	296	-125	A.P.
PM	900	9.6	4.7	251	249	425	900	505	297	-126	A.P.
Blank	950	9.2	4.7	251	250	443	951	530	302	-125	A.P.
Blank	950	9.3	4.7	250	250	449	948	533	320	-124	A.P.
PM	950	9.3	4.7	250	250	456	948	540	331	-125	A.P.
PM	950	9.2	4.7	252	250	461	948	545	332	-128	A.P.
Blank	1000	8.9	4.4	251	250	486	1001	579	334	-125	A.P.
Blank	1000	8.9	4.4	252	250	492	1001	586	328	-123	A.P.
PM	1000	8.9	4.5	251	250	499	1001	589	349	-125	A.P.
PM	1000	8.9	4.5	250	251	505	1002	595	352	-123	A.P.
PM	1000	8.9	4.5	256	250	524	1002	601	359	-125	A.P.
PM	1000	8.9	4.5	256	250	520	1001	606	369	-123	A.P.
PM	1000	8.8	4.5	250	251	520	1001	607	360	-125	A.P.
PM	1000	8.9	4.5	252	251	525	1001	610	363	-123	A.P.

[a] Conditions were monitored and logged before and after the experiment. Blank: blank experiment before combustion, PM: fluorinated acrylic polymer

[b] Reactor set temperature

[c] Inlet 1 flow rate

[d] Inlet 2 flow rate

[e] Measured temperature at each position

[f] Reactor pressure, AP: atmospheric pressure

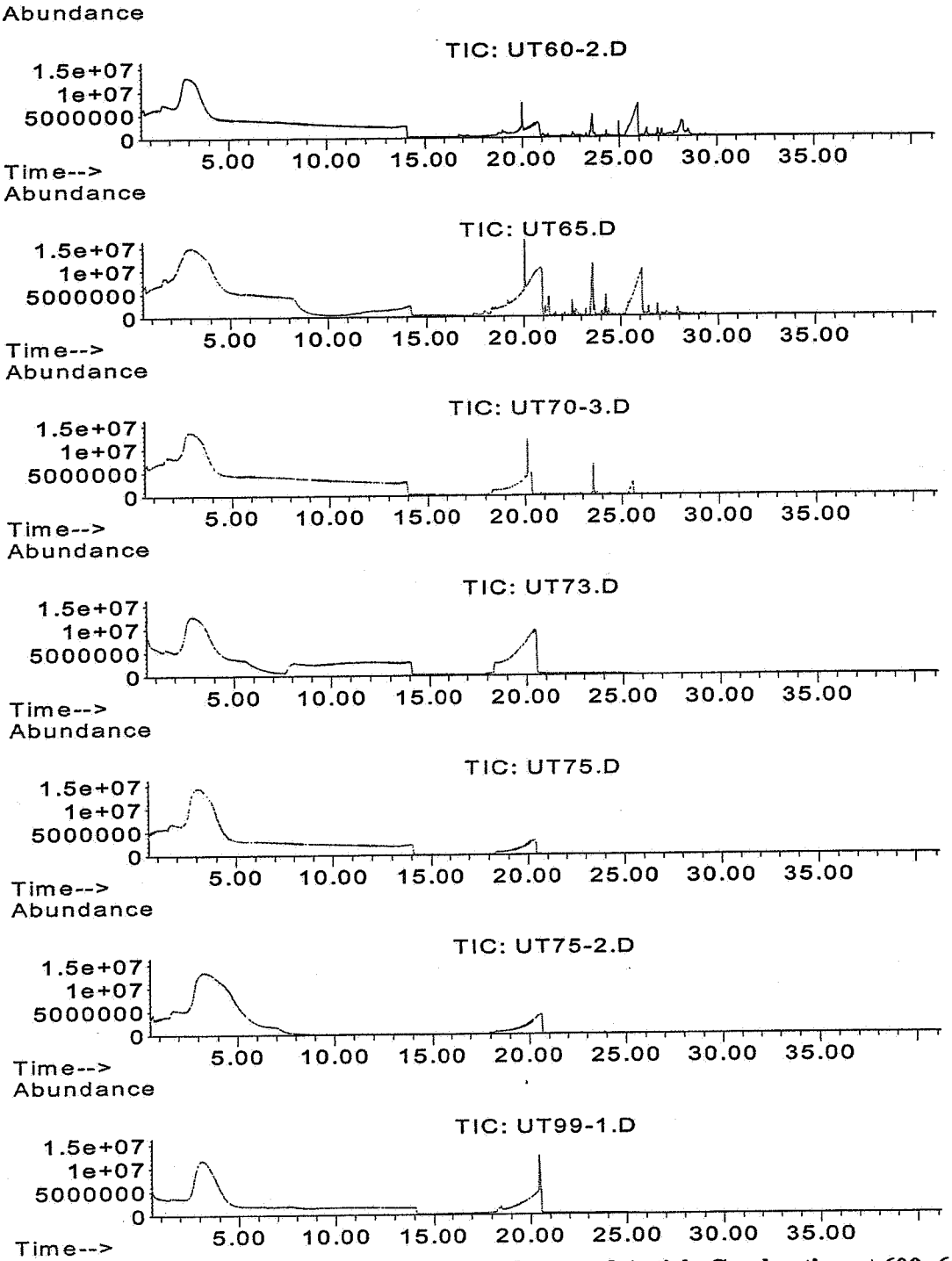

Figure A1. Total Ion Chromatogram for Untreated Article Combustion at 600, 650, 700, 725, 750, 750 (duplicate), and 1000°C

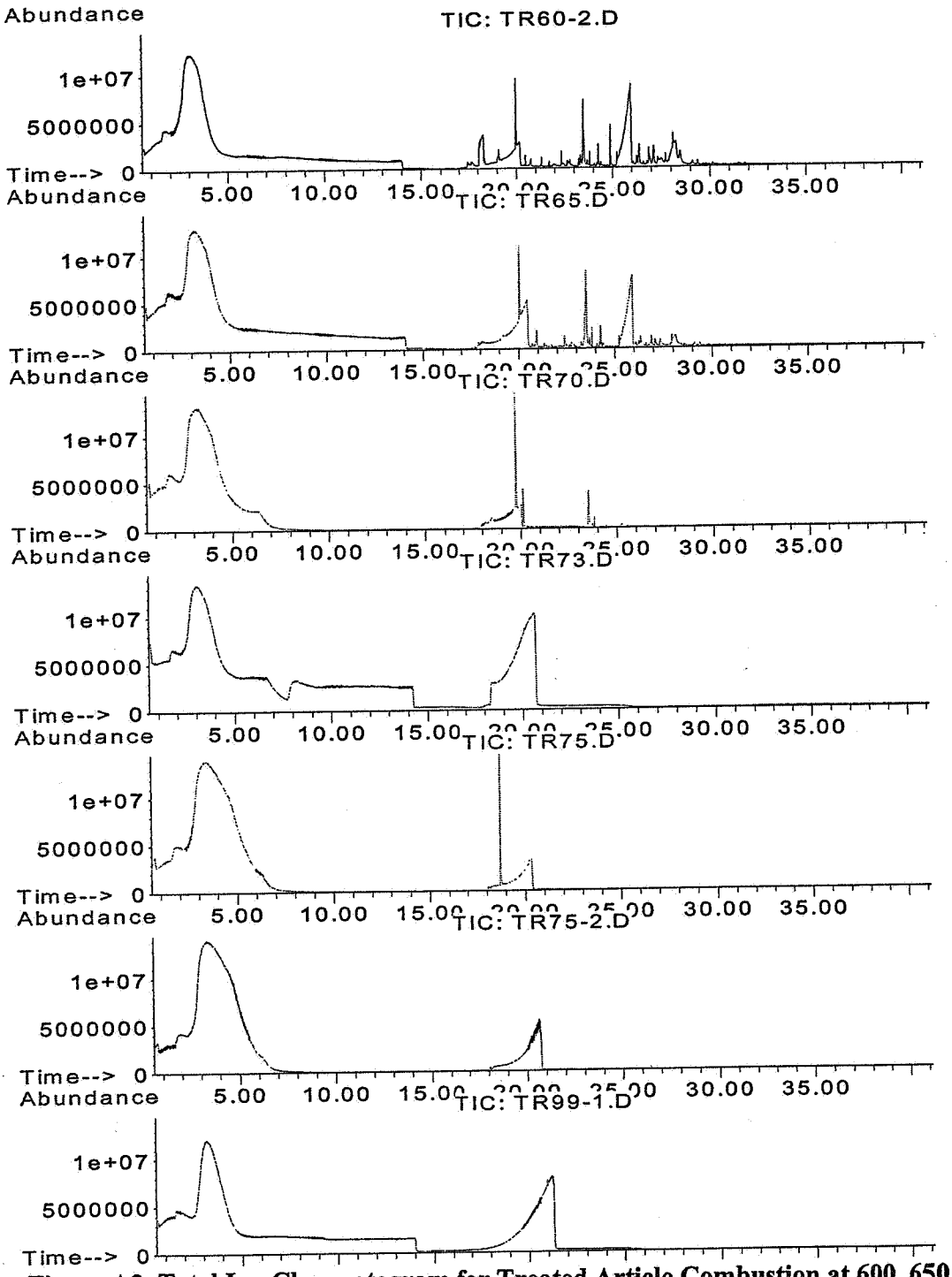

Figure A2. Total Ion Chromatogram for Treated Article Combustion at 600, 650, 700, 725, 750, 750 (duplicate), and 1000°C

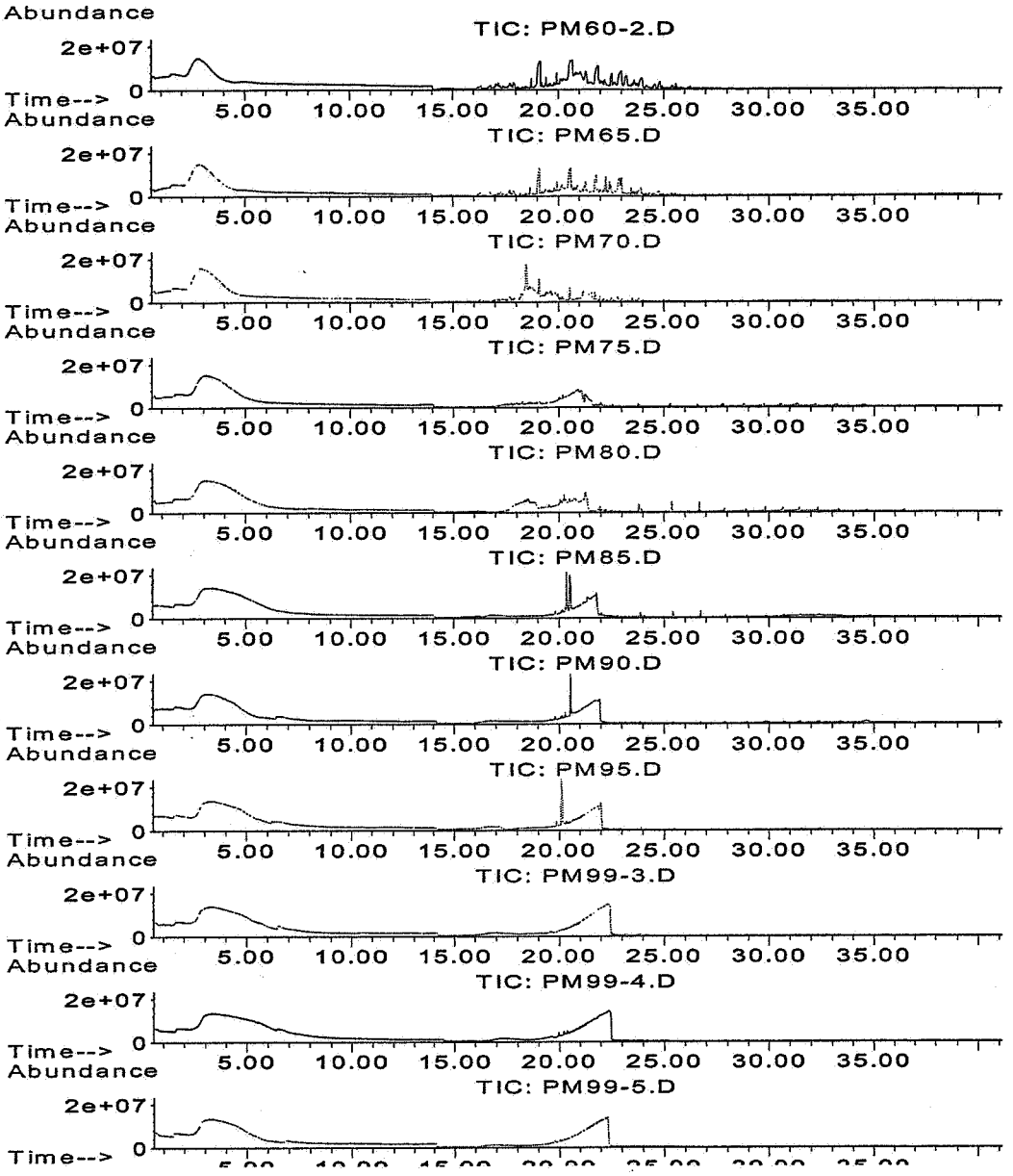

Figure A3. Total Ion Chromatogram for Fluorinated Acrylic Polymer Combustion at 600, 650, 700, 750, 800, 850, 900, 950, 1000, 1000 (duplicate), and 1000°C (triplicate)

Appendix B

Experimental Condition (Temperature and Flow Rate) and Results for PFOA, F, and Cl Aqueous Solution Analysis

Appendix B

LIST OF FIGURES

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Table B1. Experimental Condition of PFOA, F^-, and Cl^- Aqueous Solution Analysis at 1000°C (All Under Atmospheric Pressure)

Sample[a] (bef/aft)	Set T[b] °C	F. R. 1[c] mL/min	F. R. 2[d] mL/min	T 1[e] °C	T 2[e] °C	T 3[e] °C	T 4[e] °C	T 5[e] °C	T 6[e] °C	T 7[e] °C	Exit[f] °C
Sample for EXYGEN											
Blank (bef)	1000	8.8	4.5	299	300	433	998	525	302	303	24
Blank (aft)	1000	8.7	4.5	301	300	471	999	558	304	303	24
UT	1000	8.8	4.5	302	301	516	1000	597	310	299	24
UT	1000	8.8	4.4	302	301	520	1001	601	315	299	24
Blank	1000	8.8	4.5	300	302	528	1002	608	321	299	24
Blank	1000	8.9	4.4	302	302	531	1002	611	323	299	24
UT	1000	8.9	4.4	302	302	532	1001	611	324	300	24
UT	1000	8.9	4.5	302	302	534	1003	613	326	301	24
Blank	1000	8.8	4.5	301	303	536	1001	615	330	300	24
Blank	1000	8.8	4.5	301	300	538	1002	616	334	301	24
UT	1000	8.8	4.5	300	301	538	1000	617	338	301	24
UT	1000	8.8	4.5	303	303	539	1002	617	340	301	24
Blank	1000	8.9	4.5	302	301	540	1002	617	343	301	24
Blank	1000	8.9	4.5	301	302	541	1002	618	345	300	24
Blank	1000	8.8	4.5	302	302	543	1003	619	357	302	24
Blank	1000	8.9	4.5	301	302	543	1001	619	358	301	24
TR	1000	8.8	4.4	302	300	543	1001	619	358	301	24
TR	1000	8.9	4.5	301	301	543	1003	619	359	301	24
Blank	1000	8.8	4.4	300	301	543	1002	619	359	302	24
Blank	1000	8.8	4.4	302	300	543	1001	619	360	303	24
TR	1000	8.8	4.4	300	301	543	1001	620	360	302	24
TR	1000	8.9	4.4	301	302	543	1002	619	360	301	24
Blank	1000	8.8	4.4	300	300	543	1001	619	360	301	24
Blank	1000	8.9	4.4	300	300	543	1002	619	360	300	24
TR	1000	8.9	4.4	299	301	543	1003	620	360	300	24
TR	1000	8.8	4.4	300	302	543	1002	619	360	299	24
Blank	1000	8.9	4.4	302	302	543	1002	619	361	299	24
Blank	1000	8.8	4.4	302	302	543	1002	619	361	299	24
Sample for UDRI											
Blank	1000	8.8	4.5	300	299	455	1000	545	347	305	24
Blank	1000	8.7	4.5	300	299	489	1000	575	370	303	24
TR	1000	8.7	4.5	300	301	489	1001	575	371	303	24
TR	1000	8.7	4.4	301	299	500	1001	584	380	302	24
Blank	1000	8.7	4.4	301	301	525	1001	599	398	302	24
Blank	1000	8.7	4.5	302	301	524	1000	601	401	302	24

[a] Conditions were monitored and logged before and after the experiment. Blank: blank experiment before combustion, UT: untreated article, TR: treated article

[b] Reactor set temperature

[c] Inlet 1 flow rate

[d] Inlet 2 flow rate

[e] Measured temperature at each position

[f] Temperature at the downstream of aqueous solution vial exhaust line

Table B2. Aqueous Solution Analytical Results from EXYGEN[a]

Sample ID	PFOA	F^-	Cl^-	Notation
UTBK1-1	ND	ND	ND	1st jar for blank run before 1st untreated article combustion
UTBK1-2	ND	ND	ND	2nd jar for blank run before 1st untreated article combustion
UT1-1	ND	ND	ND	1st jar for 1st untreated article combustion
UT1-2	ND	ND	ND	2nd jar for 1st untreated article combustion
UTBK2-1	ND	ND	ND	1st jar for blank run before 2nd untreated article combustion
UTBK2-2	ND	ND	ND	2nd jar for blank run before 2nd untreated article combustion
UT2-1	ND	ND	ND	1st jar for 2nd untreated article combustion
UT2-1	ND	ND	ND	2nd jar for 2nd untreated article combustion
UTBK3-1	ND	ND	ND	1st jar for blank run before 3rd untreated article combustion
UTBK3-2	ND	ND	ND	2nd jar for blank run before 3rd untreated article combustion
UT3-1	ND	ND	ND	1st jar for 3rd untreated article combustion
UT3-2	ND	ND	ND	2nd jar for 3rd untreated article combustion
UTBK4-1	ND	ND	ND	1st jar for blank run after 3rd untreated article combustion
UTBK4-2	ND	ND	ND	2nd jar for blank run after 3rd untreated article combustion
BK1	ND	ND	ND	HPLC water blank
TRBK1-1	ND	ND	ND	1st jar for blank run before 1st treated article combustion
TRBK1-2	ND	ND	ND	2nd jar for blank run before 1st treated article combustion
TR1-1	ND	ND	ND	1st jar for 1st treated article combustion
TR1-2	ND	ND	ND	2nd jar for 1st treated article combustion
TRBK2-1	ND	ND	ND	1st jar for blank run before 2nd treated article combustion
TRBK2-2	ND	ND	ND	2nd jar for blank run before 2nd treated article combustion
TR2-1	ND	ND	ND	1st jar for 2nd treated article combustion
TR2-2	ND	ND	ND	2nd jar for 2nd treated article combustion
TRBK3-1	ND	ND	ND	1st jar for blank run before 3rd treated article combustion
TRBK3-2	ND	ND	ND	2nd jar for blank run before 3rd treated article combustion
TR3-1	ND	ND	ND	1st jar for 3rd treated article combustion
TR3-2	ND	ND	ND	2nd jar for 3rd treated article combustion
TRBK4-1	ND	ND	ND	1st jar for blank run after 3rd treated article combustion
TRBK4-2	ND	ND	ND	2nd jar for blank run after 3rd treated article combustion
BK2	ND	ND	ND	HPLC water blank

[a] ND: compound not detected, < 10ng/L.

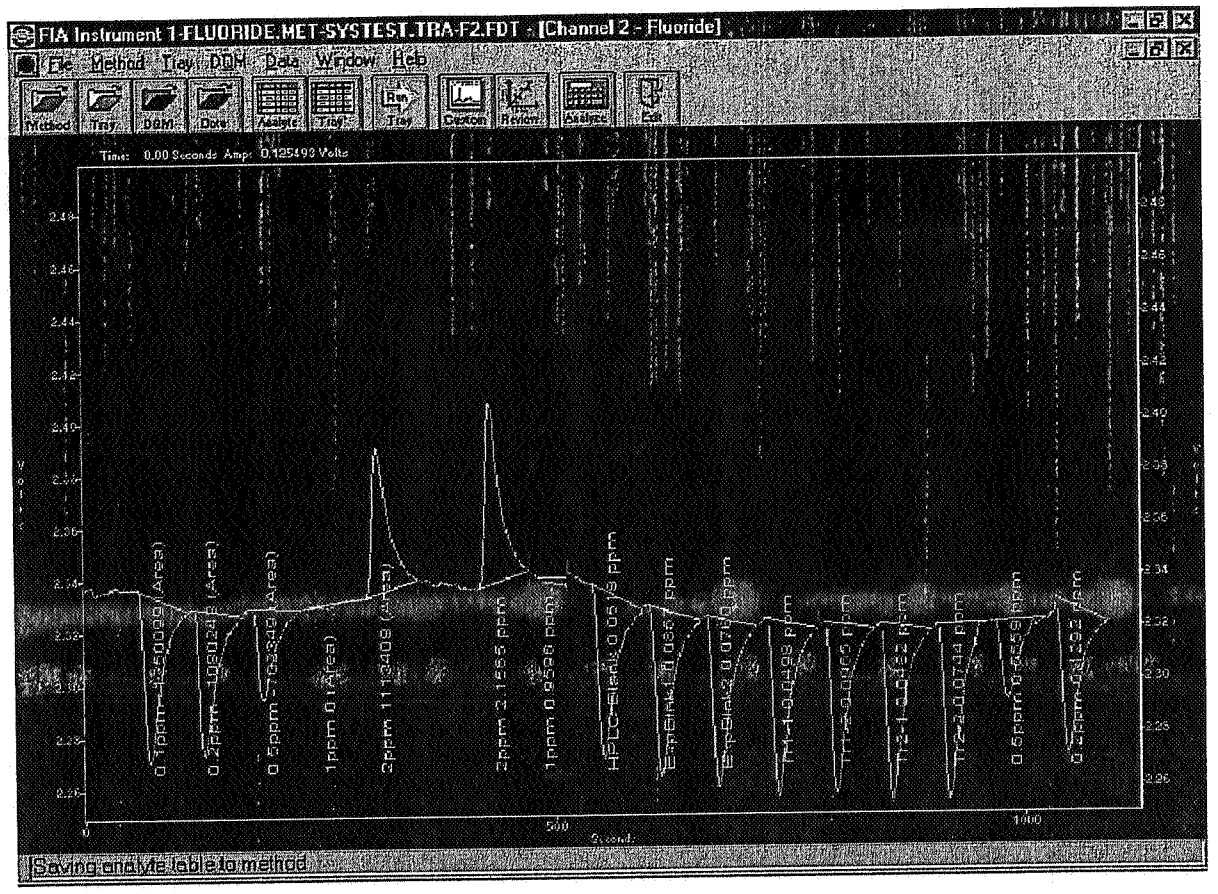

Figure B1. Fluoride Analysis Result at UDRI

Notations: HPLC Blank, ExpBlank1, ExpBlank2, Tr1-1, Tr1-2, Tr2-1, and Tr2-2 correspond to HPLC grade water, 1st and 2nd bottles of aqueous solution for blank run at 1000°C, 1st and 2nd bottles of aqueous solution for 1st treated article combustion at 1000°C, and 1st and 2nd bottles of aqueous solution for 2nd treated article combustion at 1000°C, respectively.

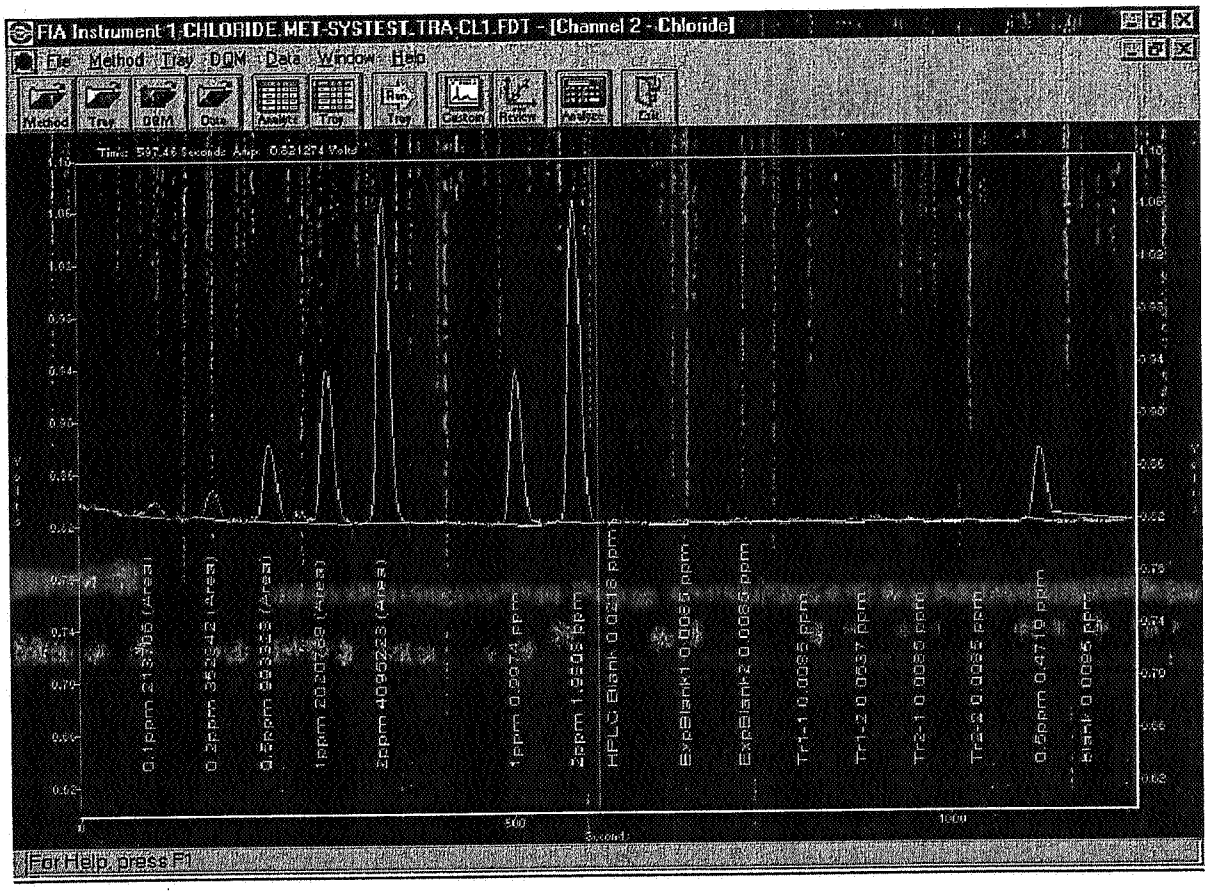

Figure B2. Chloride Analysis Result at UDRI

Notations: HPLC Blank, ExpBlank1, ExpBlank2, Tr1-1, Tr1-2, Tr2-1, and Tr2-2 correspond to HPLC grade water, 1st and 2nd bottles of aqueous solution for blank run at 1000°C, 1st and 2nd bottles of aqueous solution for 1st treated article combustion at 1000°C, and 1st and 2nd bottles of aqueous solution for 2nd treated article combustion at 1000°C, respectively.

Appendix C

Experimental Condition (Temperature, Flow Rate, and Pressure) and Total Ion Chromatogram for Telomer In-line GC/MS Analysis

Appendix C

LIST OF FIGURES

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Table C1. Experimental Condition of Telomer Combustion

Sample[a] (bef/aft)	Set T[b] °C	F. R. 1[c] mL/min	F. R. 2[d] mL/min	T 1[e] °C	T 2[e] °C	T 3[e] °C	T 4[e] °C	T 5[e] °C	T 6[e] °C	T 7[e] °C	Pres[f] °C
Blank (bef)	200	24.1	11.7	149	151	133	199	157	134	-125	A.P.
Blank (aft)	200	23.8	11.3	151	151	134	201	161	139	-123	A.P.
Telom	200	23.3	11.6	151	151	133	201	148	150	-125	A.P.
Telom	200	23.7	117	150	151	133	201	149	149	-127	A.P.
Telom	600	12.8	6.5	150	149	150	601	205	154	-125	A.P.
Telom	600	12.7	6.5	151	157	170	601	232	151	-128	A.P.

[a] Conditions were monitored and logged before and after the experiment. Blank: blank experiment before combustion, Telom: telomer sample

[b] Reactor set temperature

[c] Inlet 1 flow rate

[d] Inlet 2 flow rate

[e] Measured temperature at each position

[f] Reactor pressure, AP: atmospheric pressure

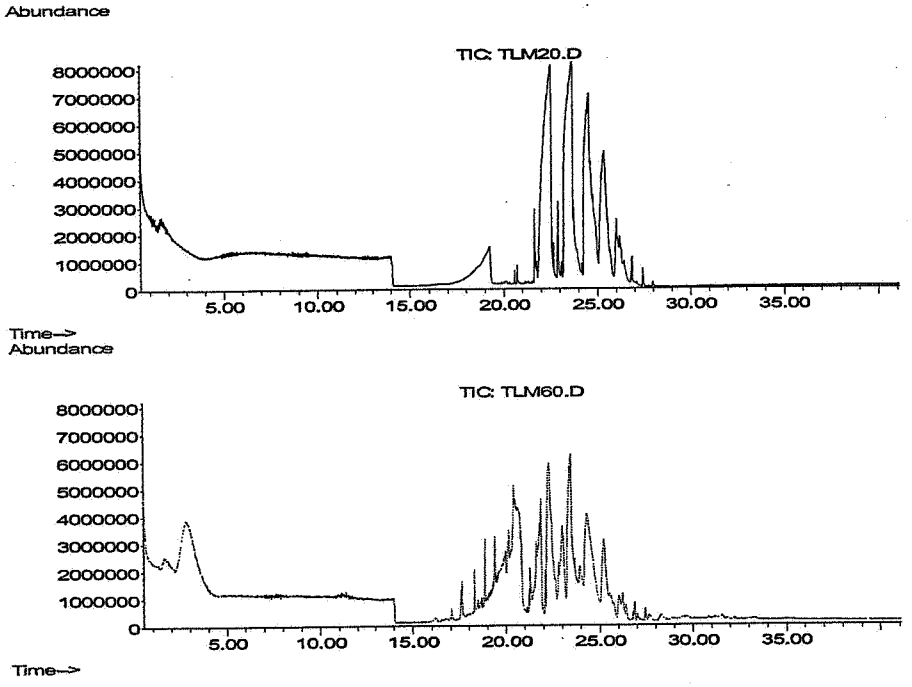

Figure C1. Total Ion Chromatogram for Telomer Combustion at 200 and 600°C

Appendix D

Experimental Condition (Temperature and Flow Rate) for VOC, CO and CO_2 Off-line GC/MS Analysis

Appendix D

LIST OF TABLES

Table D1. Experimental Condition of Off-line GC/MS VOC Analysis (All under Atmospheric Pressure)

Sample[a] (bef/aft)	Set T[b] °C	F. R. 1[c] mL/min	F. R. 2[d] mL/min	Makeup[e] mL/min	T 1[f] °C	T 2[f] °C	T 3[f] °C	T 4[f] °C	T 5[f] °C	T 6[f] °C	T 7[f] °C
Blank (bef)	1000	8.8	4.3	6.7	300	302	399	1002	486	292	302
Blank (aft)	1000	8.7	4.2	6.8	301	302	425	1002	507	297	303
UT	1000	8.7	4.2	6.8	301	302	425	1002	507	297	303
UT	1000	8.6	4.2	6.8	300	300	439	1001	513	304	303
UT	1000	8.6	4.4	6.8	300	300	439	1001	513	304	303
UT	1000	8.7	4.3	6.8	301	302	435	1002	517	311	302
UT	1000	8.7	4.3	6.8	301	302	435	1002	517	311	302
UT	1000	8.7	4.4	6.8	302	301	440	1002	522	319	302
Blank	1000	8.9	4.5	6.8	301	301	398	1002	484	282	308
Blank	1000	8.8	4.4	6.8	302	301	416	1000	500	297	304
TR	1000	8.8	4.4	6.8	302	301	416	1000	500	297	304
TR	1000	8.8	4.5	6.7	300	302	425	1001	508	307	303
TR	1000	8.8	4.5	6.7	300	302	425	1001	508	307	303
TR	1000	8.9	4.5	6.8	301	302	432	1002	514	312	302
TR	1000	8.9	4.5	6.8	301	302	432	1002	514	312	302
TR	1000	8.8	4.4	6.8	301	301	437	1001	518	318	300

[a] Conditions were monitored and logged before and after the experiment. Blank: blank experiment before combustion, UT: untreated article, TR: treated article

[b] Reactor set temperature

[c] Inlet 1 flow rate

[d] Inlet 2 flow rate

[e] Makeup gas flow rate

[f] Measured temperature at each position

Appendix E

Experimental Condition (Temperature and Flow Rate) for PFOA Transport Efficiency Test and System Steam Extraction

Appendix E

LIST OF TABLES

Table E1. Experimental Condition of PFOA Transport Test (All under Atmospheric Pressure)

Sample[a] (bef/aft)	Set T[b] °C	F. R. 1[c] mL/min	F. R. 2[d] mL/min	Makeup[e] mL/min	T 1[f] °C	T 2[f] °C	T 3[f] °C	T 4[f] °C	T 5[f] °C	T 6[f] °C	T 7[f] °C
Blank (bef)	170	12.6	6.5	6.9	171	169	170	170	214	159	165
Blank (aft)	170	12.7	6.5	6.9	170	171	170	170	214	158	165
PFOA	170	12.7	6.5	6.9	170	171	170	170	214	158	165
PFOA	170	12.8	6.5	6.9	169	169	170	171	214	158	165
PFOA	170	12.8	6.5	6.9	169	169	170	171	214	158	165
PFOA	170	12.9	6.5	6.9	171	170	170	170	214	158	166
PFOA	170	12.9	6.5	6.9	171	170	170	170	214	158	166
PFOA	170	12.8	6.4	6.9	170	170	170	171	214	158	166
Blank	300	12.7	6.3	6.9	171	172	221	201	205	300	295
Blank	300	12.9	6.5	6.9	169	169	221	299	305	302	295
PFOA	300	12.9	6.5	6.9	169	169	221	299	305	302	295
PFOA	300	12.9	6.4	6.9	169	170	222	302	306	305	296
PFOA	300	12.9	6.4	6.9	169	170	222	302	306	305	296
PFOA	300	12.7	6.4	6.9	169	170	225	302	306	300	296
PFOA	300	12.7	6.4	6.9	169	170	225	302	306	300	296
PFOA	300	12.8	6.4	6.9	169	171	225	301	306	298	296

[a] Conditions were monitored and logged before and after the experiment. Blank: blank experiment before combustion
[b] Reactor set temperature
[c] Inlet 1 flow rate
[d] Inlet 2 flow rate
[e] Makeup gas flow rate
[f] Measured temperature at each position

Table E2. Experimental Condition of Steam Extraction (All under Atmospheric Pressure)

Sample[a] (bef/aft)	Set T[b] °C	F. R. 1[c] mL/min	F. R. 2[d] mL/min	Makeup[e] mL/min	T 1[f] °C	T 2[f] °C	T 3[f] °C	T 4[f] °C	T 5[f] °C	T 6[f] °C	T 7[f] °C
1st Extract	300	4.1	8.2	7.9	300	300	299	300	311	296	298
1st Extract	300	3.8	8.2	7.4	301	300	300	299	311	294	302
2nd Extract	300	3.8	8.2	7.4	301	300	300	299	311	294	302
2nd Extract	300	3.9	8.0	8.1	299	300	300	299	305	300	298
3rd Extract	300	3.9	8.0	8.1	299	300	300	299	305	300	298
3rd Extract	300	4.6	8.4	8.0	300	300	295	301	305	305	296
4th Extract	300	4.6	8.4	8.0	300	300	295	301	305	305	296
4th Extract	300	4.1	7.7	8.3	299	300	290	301	305	305	303
5th Extract	300	4.1	7.7	8.0	299	300	290	301	305	305	303
5th Extract	300	4.1	8.0	8.1	300	299	291	301	307	305	305

[a] Conditions were monitored and logged before and after the experiment
[b] Reactor set temperature
[c] Inlet 1 flow rate
[d] Inlet 2 flow rate
[e] Makeup gas flow rate
[f] Measured temperature at each position

Appendix F

Experimental Condition (Temperature and Flow Rate) for PFOA Calibration and Detection Limit Study

Appendix F

LIST OF TABLES

Table F1. Experimental Conditions for PFOA Calibration and Detection Limit Study

Sample[a] (bef/aft)	Set T[b] °C	F. R. 1[c] mL/min	F. R. 2[d] mL/min	T 1[e] °C	T 2[e] °C	T 3[e] °C	T 4[e] °C	T 5[e] °C	T 6[e] °C	T 7[e] °C	Pres[f] atm
Blank (bef)	300	19.6	9.8	301	300	270	302	299	301	-125	A.P.
Blank (aft)	300	19.7	9.6	300	301	270	301	299	301	-125	A.P.
PFOA 1μg	300	19.6	9.8	300	301	270	301	299	301	-125	A.P.
PFOA 1μg	300	19.6	9.6	300	302	270	299	298	300	-125	A.P.
PFOA 1μg	300	19.7	9.7	300	302	270	300	301	301	-125	A.P.
PFOA 1μg	300	19.6	9.7	301	301	270	299	300	300	-120	A.P.
Blank	300	19.8	9.8	299	301	271	301	301	301	-125	A.P.
Blank	300	19.7	9.8	301	302	270	302	301	301	-123	A.P.
PFOA 5μg	300	19.8	9.8	300	302	269	300	301	301	-125	A.P.
PFOA 5μg	300	19.7	9.9	300	302	269	300	301	301	-124	A.P.
PFOA 5μg	300	19.6	9.8	300	300	270	301	301	300	-125	A.P.
PFOA 5μg	300	19.7	9.7	301	300	270	299	300	300	-123	A.P.
Blank	300	19.8	9.6	301	301	270	300	299	300	-125	A.P.
Blank	300	19.7	9.8	300	302	270	302	299	299	-125	A.P.
PFOA 10μg	300	19.7	9.6	301	302	270	300	299	302	-125	A.P.
PFOA 10μg	300	19.8	9.7	302	301	269	299	300	301	-125	A.P.
PFOA 10μg	300	19.8	9.6	301	299	270	302	299	300	-125	A.P.
PFOA 10μg	300	19.8	9.7	300	301	270	301	300	299	-125	A.P.
Blank	300	19.7	9.9	302	300	271	301	300	301	-125	A.P.
Blank	300	19.7	9.8	301	300	270	300	301	301	-128	A.P.
PFOA 50μg	300	19.8	9.8	300	301	270	301	300	301	-125	A.P.
PFOA 50μg	300	19.7	9.9	301	299	269	300	300	301	-122	A.P.
PFOA 50μg	300	19.9	9.8	299	300	269	298	301	299	-127	A.P.
PFOA 50μg	300	19.8	9.8	300	302	270	300	301	299	-125	A.P.
Blank	300	19.8	9.6	300	301	270	302	298	301	-124	A.P.
Blank	300	19.7	9.7	300	301	269	300	298	301	-120	A.P.
PFOA 100μg	300	19.8	9.7	300	302	268	298	298	301	-125	A.P.
PFOA 100μg	300	19.6	9.8	302	301	268	302	298	301	-128	A.P.
PFOA 100μg	300	19.8	9.6	299	301	270	300	301	301	-125	A.P.
PFOA 100μg	300	19.8	9.6	298	300	270	299	300	301	-122	A.P.
Blank	300	19.7	9.8	300	302	270	298	299	301	-125	A.P.
Blank	300	19.6	9.7	299	301	370	299	300	302	-124	A.P.

[a] Conditions were monitored and logged before and after the experiment. Blank: blank experiment before combustion.

[b] Reactor set temperature

[c] Inlet 1 flow rate65

[d] Inlet 2 flow rate

[e] Measured temperature at each position

[f] Reactor pressure, AP: atmospheric pressure

Appendix G

General Description of ATRS Standard Procedure, Wickbold Torch Methods for Total Fluorine, and QuikChem® Method for Fluoride and Chloride in Water

Appendix G

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G1. Thermal Decomposition of Organic Materials using the Advanced Thermal Reactor System

The University of Dayton Research Institute's (UDRI) Environmental Engineering Group (EEG) has been conducting thermal stability measurements of organic materials since 1971 beginning with a study on the products evolved from the thermal decomposition of polymers used in beverage containers [1, 2]. This early work was conducted using a system consisting of the thermogravimetric analyzer connected in series with a high-speed gas chromatograph. Since then the EEG has developed a series of specialized instrumentation systems to study the thermal decomposition of organic materials [3-8].

Background

Regardless of the material being studied a similar overall approach to measuring the thermal decomposition is used. The sample, which can be a gas liquid or solid, is thermally vaporized, mixed with flowing gas (normally dry air), and swept through a high temperature reactor. The exhaust leaving the reactor is collected and analyzed by GC/MS. The fraction of parent species remaining (destruction efficiency) and products are determined by comparing GC/MS analyses taken at relatively low reactor temperatures (where the rate of oxidation is negligible) with data obtained at higher temperatures (where the rate of oxidation is significant). Data is typically taken at ever increasing temperatures until all of the parent species and products are oxidized. For exposures where air is in great excess this typically requires temperatures on the order of 800°C with a mean residence time of 2 s.

The exposure conditions are generally defined by the mean temperature, residence time, and level of excess air (in excess, near-stoichiometric, pyrolysis). With adequate method development the residence time distribution and a more precise measure of excess air (equivalence ratio) may be defined. The exposure temperature is measured at the reactor mid-point using a thermocouple. The mean residence time (MRT) is determined from the flow rate (measured at room temperature and corrected to the reactor temperature assuming ideal gas behavior) and the volume of the reactor. The residence time distribution is taken as being sufficiently narrow that plug flow may be assumed. This is an appropriate assumption for MRTs less than on the order of 10 sec. For longer MRTs the plug flow assumption should be checked. The level of excess air for fluids (liquids and gases) is estimated from the chemical oxygen demand of the sample (assuming complete conversion to CO_2, H_2O, etc.) and relative concentrations of oxygen and sample as calculated from their measured flow rates. The estimation of excess air for solid samples is similar, though solids may not be easily introduced to the reactor system at a fixed rate. The nominal method is to evaporate small quantities of the sample using a pyroprobe, a device designed to vaporize samples by heating them at a fixed rate. The rate of evaporation from the probe can be estimated using TGA data obtained under the same conditions of sample size, atmosphere, and heating rate.

A typical flow reactor system used for thermal decomposition research is the Advanced Thermal Reactor System (ATRS) shown in Figure G1. This system is unique in that the design allows optical access to the reactor so that photochemical reactors may be conducted at high temperatures in addition to conventional thermal decomposition. As shown in Figure G1 the ATRS consists of a reactor assembly and inline analytical systems connected via a cryogenic interface. The reactor assembly consists of a thermally insulated enclosure housing the sample introduction, reactor, and transfer line systems. The reactor feed system includes two independent sample inlets; a low-volume inlet for the controlled introduction of gas- and liquid-phase samples, and a multi-purpose inlet which may be fitted with special probes for the introduction of gas-, liquid-, or solid-phase samples and heterogeneous materials. The flow through these inlets is independently controlled and connected to the reactor through heated transfer lines. The reactor is housed within its own small tube furnace and may be independently heated to 1,200°C. The furnace can accommodate reactors as large as 2cm in diameter and 25cm long. The exhaust line from the reactor is heat traced to prevent cool regions where reactor products may be lost through condensation. The

cryogenic interface is a shell and tube design in which the shell can be cooled to near liquid nitrogen temperatures (-193°C). This permits the collection of all but the lightest reactor products. The incondensable products, typically carbon monoxide and methane, can be collected at the exhaust vent in Tedlar sample collection bags for separate analysis. The analytical system used on the ATRS is a Hewlett Packard 5890/5970 GC/MS/FID. The GC oven can be fitted with dual columns for simultaneous MS and FID analysis of the reactor products. Further details of the ATRS are presented in Graham, et al. [9].

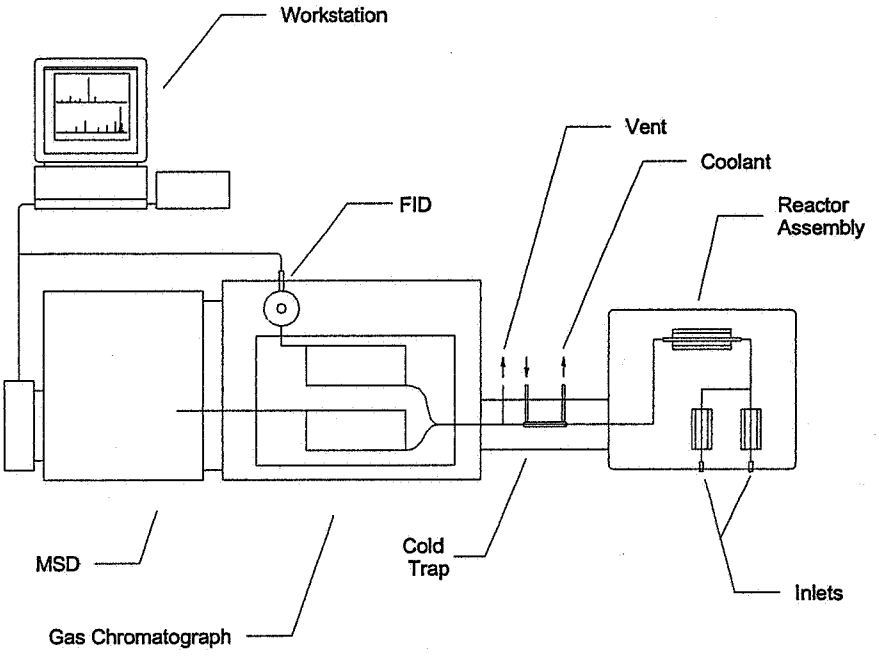

Figure G1. General Schematic of the Advanced Thermal Reactor System (ATRS).

Generalized Standard Operating Procedure

System Preparation

Prior to introducing the sample, activate set-points for the various temperatures and flow rates to ensure that the desired experimental conditions are established.

Analytical System

1. Prepare the in-line GC/FID/MS analytical subsystem in a stand-by mode with the appropriate analysis programs (temperature program, scanning ranges, detector sensitivity, etc.) set as per manufacturer's SOP.

Inlet, Exhaust Line, and Cold Trap Temperatures

2. Check the set points on the inlet temperature controllers. Observe the indicated temperatures of each controller to ensure that they are properly cycling about their respective set points.

3. Check the dial settings on the variable transformer controlling the exhaust line heaters and the exhaust line temperature to ensure that it is stable.

4. Check the dial settings on the variable transformer controlling the cold trap enclosure heater and the cold trap temperature. Observe the indicated temperature to ensure that it is stable.

Reactor Gas Feed Rate

5. Check the settings on the flow controllers to the inlet channels. Measure the total flow rate using a bubble flow meter at the cold trap vent. Adjust the total flow as needed to the desired value.

Reactor Temperature

6. Check the set point on the reactor temperature controller. Observe the indicated temperature to ensure that the controller is properly cycling about the set point.

Cold Trap Preparation and Effluent Collector

7. Check cold trap nitrogen purge is on stand-by (metering valve two turns open). Fill the coolant dewar with liquid nitrogen (or other coolant as required). Check the cold trap temperature. Adjust nitrogen flow so that the cold trap temperature is correctly set.

8. Attach a Tedlar sample collection bag to the system exhaust port. Check the sampling valve is in the VENT position.

Reactor Operation

Once the system is ready, the sample may be admitted and a test conducted.

Test Monitoring

9. While the sample is being admitted to the ATRS, monitor the cold trap temperature and coolant level. Also monitor the reactor temperature.

After the sample has been introduced to the system, continue the test monitoring for 2 minutes to ensure complete transport of sample through the system.

Post-Test Operations

10. Continue to monitor the coolant level and cold trap temperature.

11. Set the Tedlar sample bag valve to VENT, stopping the collection of exhaust.

12. Switch the reactor carrier gas OFF and the helium purge system ON. Wait for 2 minutes before proceeding.

13. Switch the analytical system from stand-by to active and hold at initial conditions.

14. Seal the cold trap vent. Observe the rise in total system pressure and adjust the flow of helium so the initial pressure is correctly set.

15. Initiate analytical system data acquisition program (i.e., switch from hold to active).

16. Switch cold trap coolant OFF.

17. Monitor analytical program as per manufacturer's SOP.

The ATRS has been used to conduct several programs for the U.S. EPA under operating guidelines developed to meet the requirements of Category III and IV Quality Assurance Program Plans (QAPPs) [10, 11].

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G2. WICKBOLD TORCH METHOD FOR TOTAL FLUORINE

1. Introduction

"The carbon-fluorine bond is exceptionally strong, and extremely vigorous conditions are needed for quantitative" analysis of fluorine in organic compounds. (Kissa, 1998) The "most vigorous" technique for measurement of fluorine in organic compounds is "combustion in an oxyhydrogen flame" referred to as the Wickbold torch. (Kissa, 1998)

2. Apparatus

A typical configuration for the Wickbold oxyhydrogen torch apparatus as described by Sweetser (1956) is shown in Figure G2.

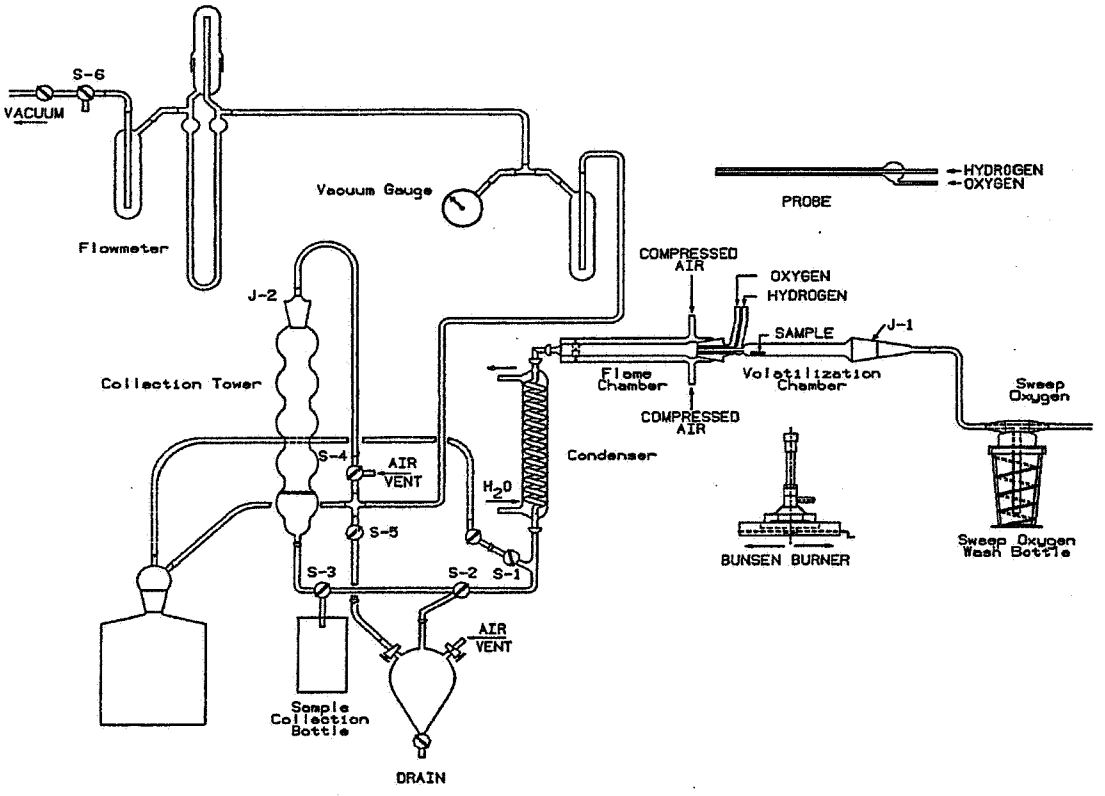

Figure G2. Wickbold Oxyhydrogen Torch Apparatus.

3. Method Description

The sample size for the standard sample boat is up to 20 mg for a solid or up to 5 mL for a liquid.

With the oxyhydrogen torch in operation, the sample is pyrolyzed or vaporized with a Bunsen burner moving on a rail below the volatilization chamber. The vapors and pyrolysis products are swept through the oxygen-hydrogen flame chamber operating at up to approximately 2000 °C to mineralize the fluorine in the sample to fluoride ion. The resulting fluoride ion is absorbed in the collection tower containing water or an alkaline solution.

The absorbed fluoride ion is measured via fluoride ion-selective electrode or ion chromatography.

The reported limit of quantitation for total fluorine via the Wickbold Torch method is 0.5 ppm (0.5 mg/kg). The accuracy of this method for determination of total fluorine in fluorinated polymers is exemplified by total fluorine values of 75.35% to 75.84% for PTFE with known total fluorine content of 76.0%. (Sweetser, 1956)

4. Safety Considerations

Use of hydrogen presents a potential fire and explosion hazard. Use of oxygen presents a potential fire hazard. Safe operation of the oxyhydrogen torch is assured by the use of specialized equipment with shielding and elaborate safety devices by well-trained personnel at a qualified laboratory.

5. References

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G3. QuikChem® Method 10-109-12-2-A, Fluoride in Water (0.10 to 5.0 mg F^-/L)

– Principle –

Fluoride is determined potentiometrically using a combination fluoride electrode and the Lachat QuikChem Flow Injection Analyzer. The fluoride electrode consists of a lanthanum fluoride crystal across which a potential is developed by fluoride ions. The reference cell is a Ag/AgCl/Cl- cell. The reference junction is of the annular liquid-junction type and encloses the fluoride-sensitive crystal.

– Interferences –

1. The polyvalent cations, Si^{4+}, Al^{3+}, and Fe^{3+}, interfere by forming complexes with fluoride. CDTA (1,2-cyclohexylene dinitrilotetracetic acid) is added to preferentially complex these cations and eliminate this interference when these concentrations do not exceed 3.0 mg Al^{3+}+/L and 20 mg Fe^{3+}+/L.

2. For US users determing Total or Total Dissolved Fluoride, the Bellack distillation is required for NPDES monitoring but is not required for SDWA monitoring.

G4. QuikChem® Method 10-117-07-1-C, Chloride in Water (0.1 to 10.0 mg Cl^-/L)

– Principle –

Thiocyanate ion is liberated from mercuric thiocyanate by the formation of soluble mercuric chloride. In the presence of ferric ion, free thiocyanate ion forms the highly colored ferric thiocyanate, of which the absorbance is proportional to the chloride concentration. Ferric thiocyanate absorbs strongly at 480 nm. The calibration curve is non-linear..

– Interferences –

1. Substances which reduce iron (III) to iron (II) and mercury (III) to mercury (II) (e.g. sulfite, thiosulfate).

2. Halides which also form strong complexes with mercuric ion (e.g. Br^-, I^-) give a positive interference.

3. If any question of interferences arise, calibration curves should be prepared in water and in the suspected interfering matrix. If the two curves differ significantly, then there is interference, and the standards must be prepared in the interfering matrix instead of in water. Calcium and magnesium ions may precipitate if present in sufficient concentration.