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Laboratory-Scale Thermal Degradation of Perfluoroalkyl Sulfonates and Perfluoroalkyl Sulfonamides

Final Report Prepared by:

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In response to a verbal and written request from:

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Final Report

Laboratory-Scale Thermal Degradation of Perfluoroalkyl Sulfonates and Perfluoroalkyl Sulfonamides

This report covers the efforts performed by the University of Dayton Research Institute (UDRI), Environmental Science and Engineering Group, Dayton, OH 45469-0132, during the period from March 2001 to December 2002. The work was conducted under a Letter of Agreement dated March 20, 2001. The work was administered under the direction of the 3M Environmental Lab, ET&SS, and the Project Monitor was

The UDRI Program Monitors were Philip Taylor and Tak Yamada.

Philip H. Taylor 1/7/03
Dr. Philip Taylor Date

Takahira Yamada 1/7/03
Dr. Tak Yamada Date

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EXECUTIVE SUMMARY

3M requested that the Environmental Sciences and Engineering Group at UDRI evaluate the thermal decomposition of the following fluorcarbon-based compounds and polymers: FC-807A and FC-1395 (C_8 perfluoroalkyl sulfonamides); $C_4F_9SO_3^-K^+$ (PFBS), and $C_8F_{17}SO_3^-K^+$ (PFOS). The overall goal of this study was to determine if incineration is a potential source of perfluoroalkyl sulfonates, e.g., perfluoroctanyl sulfonates (PFOS), which has been found in a number of wildlife tissue samples (Giesy, et al., 2001; Kannan, et al., 2001).

A laboratory-scale study roughly simulating a full-scale hazardous waste incinerator was envisioned. Based on prior experience with halogenated compounds, we initially planned to use relatively modest conditions in the primary combustion zone (ca. 400°C) to gasify the materials with more severe high-temperature (600 – 900°C), oxidative conditions representing a secondary combustion zone. TGAs of the active ingredients indicated that higher temperatures (~ 600°C) were necessary to gasify these unique materials. The sponsor also requested that the experiment be designed to detect low-level (0.1%) transformation to perfluoroalkylsulfonates in the exhaust gases from the fluorinated portions of the test compounds. The combination of these factors necessitated the use of large amounts of material (milligram quantities) and high-temperature, long duration exposures (ca. 1250°C, 40 sec) in a specially designed pyroprobe to fully gasify the material. These conditions, while representing quite severe conditions in the primary zone of an incinerator, e.g., a rotary kiln, are representative of the range of conditions that occur in a full-scale system. As such, the approach employed in the laboratory-scale combustion study is a reasonable extrapolation of a full-scale incineration study of perfluoroalkyl sulfonates and polymers that contain these active ingredients.

Combustion tests were completed for seven fluorinated alkyl sulfonyl hydrocarbons: FC-1395, FC-807A, $C_4F_9SO_3^-K^+$ (PFBS), and $C_8F_{17}SO_3^-K^+$ (PFOS) as requested by the sponsor. In-line and off-line GC/MS analyses, reactor effluent sample collection using PUF cartridges followed by LC-MS analysis, and chemical extraction of various transfer lines throughout the reactor system including the reactor itself followed by LC-MS analysis were conducted to investigate the following: 1) the extent of conversion of the active ingredients, 2) the formation of fluorinated organic incomplete combustion byproducts, and 3) the extent of conversion of the sulfur to sulfur oxides.

The data presented herein clearly show that incineration of FC-1395 and FC-807A does not release perfluorinated alkyl sulfonates. This conclusion is based mainly on the LC/MS measurements, but was substantiated by the extracted ion analysis that showed negligible 67-SOF ion indicating negligible amounts of volatile sulfonate-containing degradation products. Sulfur recoveries varied from 40 to 120%, depending on the fluorocarbon or fluorocarbon polymer combusted. The dominant sink for sulfur was SO_2. GC/MS analysis of perfluorinated alkyl sulfonate precursors indicated that such precursors were not present in the reactor effluent. This finding is consistent with the LC/MS measurements, and strongly suggests that the C-S bond was completely destroyed (and did not reform) in the combustion tests.

Several fluorinated organic intermediates were observed in the reactor effluent. These compounds were limited to fluorinated alkanes, fluorinated alkenes, and fluorinated aromatics. Higher molecular weight fluorinated polycyclic aromatic hydrocarbons were not observed.

The data from this laboratory-scale incineration study indicates that properly operating full-scale municipal or hazardous waste incineration system can adequately dispose of these unique materials. Incineration of these fluorinated compounds is not likely to be a significant source of perfluorinated alkyl sulfonates into the environment. Fluorinated organic intermediates are also unlikely to be emitted from these facilities.

1. Background

The destruction efficiency (DE) of principal organic hazardous constituents (POHCs) is dominated by the temperature, time, fuel (waste)/air mixing, and fuel/air stoichiometry (excess air) experienced by the POHCs in the high temperature zones of incinerators (Dellinger, et al., 1991). Numerous calculations and experiments have shown that emissions of undestroyed, residual POHCs are kinetically, not thermodynamically controlled (Tsang and Shaub, 1982; Trenholm, et al., 1984; Dellinger, et al. 1991). As a result, accurate assessment of POHC emissions require thermal stability testing and cannot be accurately modeled based on thermodynamic equilibrium calculations.

Simple conceptual and more complex computer models indicate that gas-phase residence time and temperature in the post-flame zones of incinerators control the relative emissions of most POHCs (Clark, et al., 1984; Dellinger, et al., 1986; Dellinger, et al. 1991). This is because all molecules entering the flame zone of an incinerator are destroyed completely to thermodynamic endproducts and only the minute fraction escaping the flame zone is actually emitted from the facility. Once in the post-flame zone, gas-phase thermal decomposition reactivity in the presence of the major gas-phase constituents of this zone control the rate of POHC destruction and formation and destruction of products of incomplete combustion (PICs).

If all POHCs in a given waste stream are volatilized at approximately the same rate, they will experience the same post-flame gas-phase residence time, temperature, and stoichiometry history (relative concentrations of POHC, oxygen, and other major gas-phase constituents as the POHCs traverse this zone). This means that gas-phase thermal stability of POHCs (as determined under a standardized set of conditions) may be used to predict their relative incinerability. The temperature for 99% destruction at 2.0 seconds gas-phase residence time, [T_{99} (2)(°C)] has been used previously to rank the thermal stability of POHCs (Taylor, et al., 1990). Other residence times or levels of destruction may be used to develop a ranking. However, laboratory data indicate that although absolute POHC DEs are dependent upon time and temperature, relative DEs are largely insensitive to these parameters (Dellinger, et al., 1984; Graham, et al., 1986; Taylor and Dellinger, 1988). On the other hand, stoichiometry has been shown to be a significant variable in determining relative stability (Graham, et al., 1986; Taylor and Dellinger, 1988; Taylor, et al., 1991).

Experimental and theoretical considerations suggest that various flame zone failure modes exist that may cause residual POHCs to be emitted from a facility. The most prominent of these are thermal quenching and waste/air mixing failure modes. Even though a facility may be operating under nominal excess air conditions, poor waste/air mixing or thermal quenching zones due to poor heat transfer at incinerator surfaces will result in conditions where the rate of POHC destruction is low and PIC formation is favored. Consequently, it is believed that gas-phase thermal stability as characterized under oxygen-starved conditions is an effective predictor of POHC relative incinerability.

The UDRI thermal stability-based incinerability ranking was initially published in 1990 with further development published in1991 (Taylor, et al. 1990; Dellinger, et al., 1991). The US-EPA has evaluated the UDRI gas-phase thermal decomposition kinetic rankings on both the pilot and

full-scale as a basis for determining POHC incinerability. Pilot-scale studies (Carroll, et al., 1992) of an eleven-component hazardous waste mixture under thermal failure and worst-case conditions (encompassing three failure-promoting conditions resulting in lower kiln-exit temperature, larger charge mass, and lower H/Cl ratio than the baseline set of conditions) both produced statistically significant correlations between product emission concentrations and their gas-phase thermal stability rankings. For the thermal failure tests, correlations above the 99% confidence interval were observed. Full-scale studies (Dellinger, et al., 1993) of a seven-component hazardous waste mixture indicated that thermal failure and waste/air mixing failures also produced statistically significant correlations. Based on median destruction and removal efficiencies (DREs), the data indicated that both the mixing and thermal failure modes produced statistically significant correlations between product emission concentrations and their gas-phase thermal stability rankings.

3M Company requested that the Environmental Sciences and Engineering Group at UDRI evaluate the thermal decomposition of the following fluorcarbon-based compounds and polymers: FC-807A and FC 1395 (C_8 perfluoroalkyl sulfonamides): $C_4F_9SO_3^-K^+$ (PFBS), The overall goal of this study was to determine if incineration is a potential source of perfluoroalkyl sulfonates, e.g., perfluoroctanyl sulfonates (PFOS), which has been found in a number of wildlife tissue samples (Giesy, et al., 2001; Kannan, et al., 2001).

This report is broken into eight sections. The first four sections describe the background of our experience in incineration research, phase I: the initial test protocol and project objectives, phase II: the method development work, and phase III: the revised test protocol. Sections five and six describe the experimental results followed by an interpretation of the results, respectively. Section seven gives conclusions and recommendations. Section eight provides a list of references. An appendix contains the following auxiliary information: 1) a timeline of the phase I, phase II, and phase III studies and the actual dates of the combustion tests, 2) the phase II final report and raw data, 3) the phase III test protocol and addendum, 4) the 3M analytical report and 5) a spreadsheet linking the UDRI combustion tests with the 3M Analytical results.

2. Phase I: Objectives and Test Protocol

The objectives of this program were the following:

1. To determine if perfluoroalkylsulfonyl compounds can form combustion products that either are perfluoroalkyl sulfonates or are precursors of perfluoroalkyl sulfonates. Precursors are compounds that could form perfluoroalkyl sulfonates through transformation reactions likely to occur in the environment.

2. I dentify the major organic combustion products of perfluoroalkylsulfonyl compounds.

3. Determine if the sulfur present in the samples is quantitatively converted to sulfur dioxide and/or thionyl fluoride (SOF_2) and sulfuryl fluoride (SO_2F_2) at high temperature, fuel-lean combustion conditions.

The development of the test protocol was based on the use of batch-charged continuous flow reactors developed at UDRI to study the thermal stability of organic materials (Rubey and Carnes, 1985, Rubey and Grant, 1988). Briefly, these systems accept a small quantity of material (typically less than 1 mg). The sample and its decomposition products are volatilized, mixed with flowing dry air, transported through a high temperature quartz tubular reactor where the sample vapors are thermally stressed under controlled conditions of time, temperature, and excess air level. The materials surviving this exposure are then passed onto an in-line gas chromatography/mass spectrometry (GC/MS) system for analysis.

Quantification of parent species is based on transport and analysis of known quantities under non-destructive conditions. Typically, products are quantified using the response factor of the parent compound or the major parent compounds if from a complex mixture. In this study, the analytical focus will be identification of stable fluorinated organic intermediates and the quantification of sulfur oxides in an attempt to recover 100% of the initial sulfur in the sample. Sulfur quantification will be performed using a mass selective detector (MSD). Consideration was also given to the use of a sulfur-specific detector that responds only to sulfur atoms. However, due to the universal nature of the MSD, i.e., its ability to detect both sulfur and fluorinated organic compounds, it was decided that the MSD would be satisfactory for these experiments.

Every sample presents its own unique set of challenges. In the case of the 3M samples the unknowns in establishing the test protocol centered around the issue of transportability. Specifically, transporting the sample to the reactor from the sample inlet and the products from the reactor to and through the analytical sub-systems. For example, it is likely that the test sample will decompose rather than evaporate and the central issue becomes whether the products from this decomposition process can be transported under acceptable conditions. Consequently, developing the test protocol for the 3M samples focused on the issues of sample feed and product transport and analysis.

The first step in any gas-phase thermal stability analysis is converting the sample into a vapor where it is mixed with the desired carrier gas and transported through the reactor system by the

bulk flow of the process stream. When working with a relatively uncharacterized sample, it is common practice to perform a thermogravimetric analysis (TGA) in oxidizing (air) and inert (nitrogen or helium) atmospheres to determine the temperature range needed to gasify the sample. This preliminary information was used to determine if the phase change is simple evaporation or decomposition and to determine if the sample deposits a non-volatile residue.

With the temperature range needed to gasify the sample established, a series of relatively simple tests was performed to determine if the gasification products could be transported under nominal flow reactor conditions. While the sample inlet systems of the UDRI reactors can be routinely heated to 400°C (with transient heating as high as 600°C), the sample transport lines to and from the reactors are typically limited to 250-300°C. Experience has shown that under these conditions most organic compounds of interest can be transported without inducing thermal reactions thereby preserving the fidelity of the samples flowing from the inlet system to the reactor and the product stream flowing from the reactor to the analytical sub-systems. A key issue to be evaluated in this study will be the transport of the PFOS/PFBS and its precursors from the gasification system to the high-temperature reactor and from the reactor to the analytical sub-systems.

The System for Thermal Diagnostic Studies (STDS) was used to perform the incineration study described herein. An overall schematic of the system is shown in Figure 2.1 The STDS is a modular, continuous, in-line reactor system that allow researchers to simulate incineration processes and perform exhaustive analyses of the output for about one-tenth the cost of full-scale tests. The instrument consists of several major components: a thermal reaction compartment; a transfer line; an analytical gas chromatograph (GC), a mass selective detector and a computer workstation. The STDS has been used to perform many types of combustion studies. The STDS has been very successful at predicting air emissions from the incineration of hazardous materials, allowing prior knowledge of the risks associated with burning a given waste.

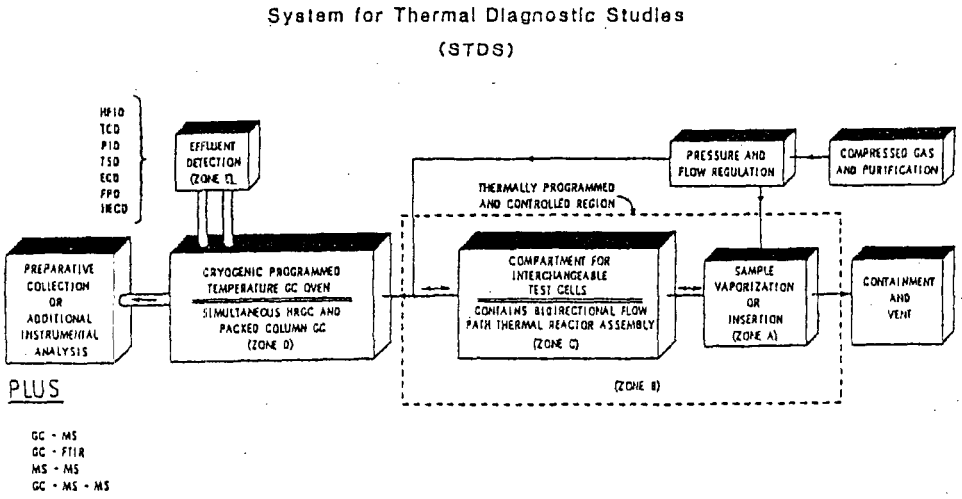

Figure 2.1. Schematic of the System for Thermal Diagnostic Studies

Initially, the Advanced Thermal Photolytic Reactor System (ATPRS) was selected for this study. To satisfy the analytical requirements for PFOS/PFBS detection by LC/MS analysis at 3M Environmental Laboratory, we determined that relatively large amounts of sample, 0.5 to several mg, had to be gasified in the actual experiments. This amount of sample was much larger than initially estimated (ca. 10 to 100 μg) and could not be gasified with the inlet available with the ATPRS. Preliminary experiments also demonstrated that higher gasification temperatures (> 400°C) were necessary to rapidly gasify the fluorocarbon-based samples. As such, the STDS, equipped with a high-temperature pyroprobe that can gasify milligram quantities of material, was selected for the actual combustion tests.

In the original protocol, we originally planned sample combustion with a liquid hydrocarbon fuel (e.g., n-octane). Subsequently, it was determined that a substitute was necesary because the liquid hydrocarbon fuel originally proposed required a much larger amount of oxygen (air) to obtain stoichiometric oxidation and it was impossible to maintain the required residence time of 1-2 seconds in the reactor under stoichiometric or excess air environments. Methane has the lowest chemical oxygen demand of any hydrocarbon fuel and is a satisfactory replacement. We decided instead to use methane as a fuel if the sample is hydrogen deficient and requires hydrogen source to convert F to HF, otherwise fuel will not be introduced to the reactor.

In the original protocol, we also proposed to conduct combustion tests at three temperatures (600, 750, and 900°C). Preliminary combustion tests with several samples indicated that many combustion byproducts were formed at 600°C, but those combustion byproducts were not observed at higher temperature (750 and 900°C) and the GC/MS total ion chromatograms for these higher temperatures were very similar. Therefore it was decided that two temperatures are sufficient to analyze the combustion phenomena of the selected samples (600 and 900°C).

3. Phase II: Method Development

The following method development tests were performed in phase II:

1. Verify that C_4 and C_8 perfluoroalkyl sulfonates can be gasified and transported through the UDRI thermal instrumentation system.
2. Establish recovery efficiencies and detection limits for stable sulfur compounds and PFOS precursors. The sulfur compounds would include but not be limited to SO_2, SOF_2, and SO_2F_2. PFOS precursors would include but not be limited to perfluorobutane sulfonyl fluoride (PBSF) and perfluorooctane sulfonyl fluoride (POSF).
3. Establish recovery efficiencies and detection limits for volatile C_1-C_4 fluorocarbons.
4. Develop a quantitative method of sampling the reactor effluent. ORBO PUF cartridges (Supelco, Inc.) will be used for sampling PFOS and its precursors from the reactor effluent.

This section summarizes the results. Calibration curves and detection limits for SO_2, SOF_2, SO_2F_2, POSF, PBSF, and C_3F_6 (hexafluoropropene (HFP)) have been established. The transport efficiency for each compound through the STDS was also examined. Verification that the C_4 and C_8 perfluoroalkyl sulfonates can be gasified and transported through the system was performed following the completion of the combustion tests. This decision was made based on the potential contamination of the system had the transport tests been done prior to the combustion study. PUF cartridge sampling of the reactor effluent was established as part of the revised phase III protocol. HFP was selected as the surrogate volatile fluorocarbon due to the lack of availability of CF_4 and CF_3H from gas suppliers. The linear fit equations for each sample, their linear correlation coefficients (R) and detection limits are tabulated in Table 3.1. Further details regarding these calibration curves are available in the Phase II report.

Table 3.1. Linear Fit Equations and Detection Limits

Sample Name	Linear Fit (Y: peak area, X: concentration (ppm))	R	Detection Limit (ppm)
SO_2	Y = 5.8813E3* X - 3.8541E5	0.9971	78.5
SOF_2	Y = 8.3335E3* X - 7.0267E4	0.99941	30.3
SO_2F_2	Y = 1.0331E4*X + 1.8273E6	0.99708	20.1
POSF	Y = 1.0423E5*X – 8.4043E5	1.0	14.1
PBSF	Y = 1.564E5*X + 1.338E6	0.998	10.0
HFP	Y = 1.4975E4*X - 2.8253E6	0.9997	3.9

The transport efficiency of each standard was estimated by comparing the measured sample peak area obtained when the sample was injected into injection port in GC1 and passed through combustion reactor and transfer line (system transport) with that obtained when the sample was injected directly into the injection port of GC2 (direct injection).

Table 3.2. Transport Efficiency

	System Transport			Direct Injection			Efficiency
	Peak Area			Peak Area			(%)
Sample	1st	2nd	AVG (1)	1st	2nd	AVG (2)	(1)/(2)×100
SO_2	9130332	8980717	9055525	11952302	11762267	11857285	76.4
SOF_2	25244352	25203780	25224066	24862639	24773683	24818161	101.6
SO_2F_2	86850304	85572809	86211557	84435720	79738316	82087018	105.0
POSF	1280370	1228718	1254544	1064431	1067947	1066189	117.7
PBSF	159824697	148389773	154107235	25091128	25284200	25187664	611.8
HFP	148679354	145606343	147142849	148372504	142271896	145322200	101.3

As illustrated in Table 3.2, the transport efficiencies for SOF_2, SO_2F_2, and HFP were within analytical error. An uncertainty of ±10% is reasonable for this type of analysis. That for POSF was slightly higher, but is nonetheless acceptable. That for SO_2 was around 76%. The SO_2 standard was analyzed as a two-component mixture with SOF_2. Since the transport efficiency for SOF_2 was nearly 100%, the results indicate some sample losses for SO_2 through the reactor and transfer lines. Because SO_2 is expected to be one of the major combustion byproducts, we will repeat the efficiency test at the onset of the actual combustion tests (see section 5.1 SO_2 Transfer Efficiency Test). We will estimate a SO_2 correction factor based on SO_2 efficiency test results to compensate for its measured concentration during the Phase III study. The efficiency for PBSF was not consistent between the two injection methods. The cause of this discrepancy was discussed with other analytical specialists in our group. The major cause may be a mixing problem of this sample with the solvent, dichloromethane. PBSF is the only liquid phase sample among the six standards. Each time PBSF was diluted with dichloromethane in the GC vials, it was shaken thoroughly in an attempt to obtain a uniform mixture. The density of PBSF is unknown, but expected to be heavier than dichloromethane. This may have caused some settling of the PBSF at the bottom of vials during preparation of the standards. The transport efficiency of PBSF will be re-examined as well as the PBSF calibration if the Phase III combustion tests indicate this is an important combustion intermediate. Further details of the initial calibration and transport efficiency tests can be found in the Phase II report provided in the Appendix.

4. Phase III: Revised Test Protocol

The combustion tests consisted of 8 separate tests as listed below:

1. SO_2 Transfer Efficiency Tests,
2. Laboratory Spike Analysis for PFOS and PFBS,
3. Heated Blank Combustion Test,
4. Combustion Tests for FC-1395, FC-807A, , PFBS, and PFOS,
5. Heated Blank Combustion Test (repeat),
6. Transfer Efficiency Test for L-16271, PFBS, and PFOS,
7. Sulfur Recovery Analysis as SO_2,
8. Extracted Ion Analysis.

Specific attention was being given to the potential formation of PFOS and PFBS during the incineration of these materials. In-line and off-line GC/MS analysis, PUF (polyurethane foam) collection of the reactor effluent and chemical extraction of the reactor and associated transfer lines were conducted. In the latter two tests, the PUF cartridges and the extracts were delivered to 3M for analysis of PFOS, PFBS, and potassium bis imide by LC/MS. Prior to the sample combustion analysis, the transfer efficiency for SO_2 was reexamined and the laboratory spike analysis for PFOS and PFBS was performed. A heated blank line analysis was performed at the onset of the sample combustion tests. After the combustion tests, another heated blank line analysis was performed. Transfer efficiency tests for , $C_4F_9SO_3^-K^+$ (PFBS), and $C_8F_{17}SO_3^-K^+$ (PFOS) were performed at the conclusion of the combustion tests. Due to resolution issues regarding the in-line sampling approach, the sulfur recovery rate as SO_2 was reanalyzed using off-line GC/MS analytical results.

Further details are provided in the Phase III test protocol and addendum that are given in an appendix to this report. The 3M analytical report (LIMS Nos. E02-0820, E02-0821, E02-0822, E02-0839, E02-0840, E02-0867, E02-0895, E02-0896, E02-0898, E02-0899, E02-0916, E02-0917, E02-0926, E02-0968, E02-0969, E02-0970, and E02-0971) is also provided in an appendix to this report. It should also be noted that the PFOS, PFBS, and data were not corrected for recovery from the PUF cartridges. Spike recoveries for PFBS and PFOS were ca. 80% with 1 μg addition of these compounds and ca. 90% with 10 μg addition of these compounds.

5. Experimental Results

5.1. SO_2 Transfer Efficiency Test

The SO_2 transfer efficiency tests conducted in Phase II was repeated in Phase III to confirm the Phase II results. The results are shown in Table 5.1.1. The SO_2 standard was analyzed as a two-component mixture with SOF_2. SO_2 transport efficiency was 83.7%, slightly higher than previous results, 76.4%, which gives average value of 80.1%. The transport efficiency for SOF_2 was again nearly 100%.

Table 5.1.1. Transport Efficiency Test Results

	System Transport			Direct Injection			Efficiency
	Peak Area			Peak Area			(%)
Sample	1st	2nd	Average (1)	1st	2nd	Average (2)	(1)/(2)×100
SO_2	8300590	8433620	8367105	10134575	9995499	10065037	83.7
SOF_2	21346398	20309703	20828051	19612747	20444301	20028524	101.9

5.2. Laboratory Spike Analysis for PFOS and PFBS

PFOS and PFBS were dissolved with 10 ml methanol (Aldrich, HPLC grade) and 1 μl of solution was placed into a reactor (4 mm (i.d.) × 6 mm (o.d.) × 7 cm length) and dried by blowing high purity nitrogen. The amount of samples used is shown in Table 5.2.1. After the drying process, the transfer lines were assembled and the samples were extracted using 5.5 ml of methanol that was also used to dissolve the samples.

Table 5.2.1. Net Amount of Sample Loaded

Sample	Net Weight (mg)	Solvent Amount (ml)	Amount Injected (μl)	Net Amount of Sample Loaded (μg)
PFOS	10.02	10	1.0	1.0
PFBS	9.78	10	1.0	1.0

Tables 5.2.2 and 5.2.3 show the extraction results for PFOS and PFBS laboratory spike analysis, respectively. The combined first and second extracts recovered 149% of the PFOS and 86% of the PFBS. In addition, 0.08 μg of PFOS, equal to 8% of the PFBS added, was recovered from the PFBS spiked reactor. The excess PFOS recovery, and the presence of PFOS in the PFBS spike is evidence of possible cross contamination. The possible source of the cross contamination is the 1/8th inch tubing which connects the reactor and collection vial shown in Figure 2 in the Phase III protocol. A new reactor/transfer line was used for each sample, but the tubing in the extraction system was repeatedly used after cleaning using reagent grade alcohol and acetone.

Table 5.2.2. PFOS Laboratory Spike Analysis

Sample Extracts	PFOS (pg/μl)	PFOS (μg)	PFBS (pg/μl)	PFBS (μg)
PFOS 1st Extracts	232	1.6	<10.1	<0.065
PFOS 2nd Extracts	40.5	0.28	<10.1	<0.065

Table 5.2.3. PFBS Laboratory Spike Analysis

Sample Extracts	PFOS (pg/μl)	PFOS (μg)	PFBS (pg/μl)	PFBS (μg)
PFBS 1st Extracts	14.7	0.10	146	0.93
PFBS 2nd Extracts	<10.0	<0.68	10.2	0.065

5.3. Heated Blank Combustion Analysis

The heated blank reactor/transfer tubing was analyzed to examine if there was any system contamination including PFOS and PFBS for the reactor temperature at 600 and 900°C prior to series of combustion tests. Four analyses, in-line GC/MS analysis, PUF collected off-gas sample analysis, off-line GC/MS analysis using Tedlar bag, and reactor/transfer line system extraction using methanol were conducted. The PUF sample collection and methanol extraction of condensed phase material were prepared and sent to 3M Environmental Laboratory for analyses. The in-line GC/MS was mainly used to analyze compounds equal to or heavier than C_6 compounds and off-line GC/MS was used for lighter compounds including SO_2. PUF sample and methanol extracts were analyzed for , PFBS, and PFOS detection. The experimental setup, reactor/transfer-line configuration, and experimental procedure followed the Phase III test protocol. The phase III test protocol and addendum can be found in the appendix to this report.

5.3.1. In-line GC/MS Analysis

Table 5.3.1 and 5.3.2 show the flow profile and carrier flow volume used for the heated blank analysis at 600 and 900°C, respectively. Of the total gas flow, 1 ml/min was introduced to the in-line GC/MS and the remainder introduced to either the PUF cartridge or the Tedlar bag for off-line analyses. A simple 1/16 in. tee was used as the flow splitter. Air was flowed to both the pyroprobe and reactor during the test except during the last time period, where helium was necessary to purge the pyroprobe and to perform the in-line GC/MS analysis. A HP5890A/5970B series GC/MS with a DB-5 MS capillary column (30 m length, 0.25 mm i.d., Agilent Technologies, Inc.) was used for the in-line GC/MS analyses. The in-line GC/MS was operated at constant pressure (10 psi). The MS was auto-tuned with perfluorotributylamine (PFTBA) and operated at an electron multiplier setting of 2000 in the scanning mode sweeping a mass range from 45 to 550 m/z. Figures 5.3.1 and 5.3.2 show total ion chromatograms for reactor temperatures of 600 and 900°C, respectively. The chromatogram shows only background noise and no contamination was found for either temperature. The background noise dropped to an apparent zero level due to the relatively high signal threshold (2500). This high threshold was used in anticipation of a high background noise level that arises from the presence of significant amounts of condensed phase combustion byproducts. This expectation was confirmed and is consistent with the large amounts of fluorochemicals that were injected into the combustion system.

Table 5.3.1. Flow Rate Profile for Heated Blank Analysis at 600°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)	Total Flow Rate (ml/min)	Total Volume (ml)	Sampled Volume[d] (ml)
0 – 120	10.5	0.80	11.30	22.60	20.60
120 – 130	10.5	0.80 → 4.63[a]	11.30 → 14.63	2.16	1.99
130 – 140	10.5	4.63	15.13	2.52	2.35
140 – 160	9.03 (He)[b]	4.53 (He)[c]	13.56	4.52	4.19
			Total Volume (ml)	31.80	29.13

[a] Linear increase (approximate). [b,c] Switched to helium for sweep. [d] Sampled volume for PUF and Tedlar bag collection.

Table 5.3.2. Flow Rate Profile for Heated Blank Analysis at 900°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)	Total Flow Rate (ml/min)	Total Volume (ml)	Sampled Volume[d] (ml)
0 – 150	7.60	0.70	8.30	20.75	18.25
150 – 160	7.60	0.70 → 4.63[a]	8.30 → 12.23	1.71	1.54
160 – 170	7.60	4.63	12.23	2.04	1.87
170 – 190	6.54 (He)[b]	4.53 (He)[c]	11.07	3.69	3.36
			Total Volume (ml)	28.19	25.02

[a] Linear increase (approximate). [b,c] Switched to helium for sweep. [d] Sampled volume for PUF and Tedlar bag collection.

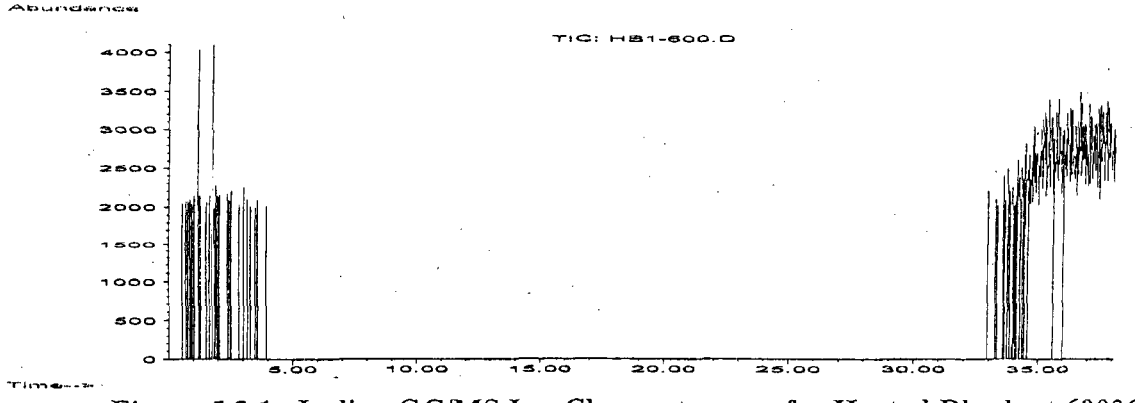

Figure 5.3.1. In-line GC/MS Ion Chromatogram for Heated Blank at 600°C

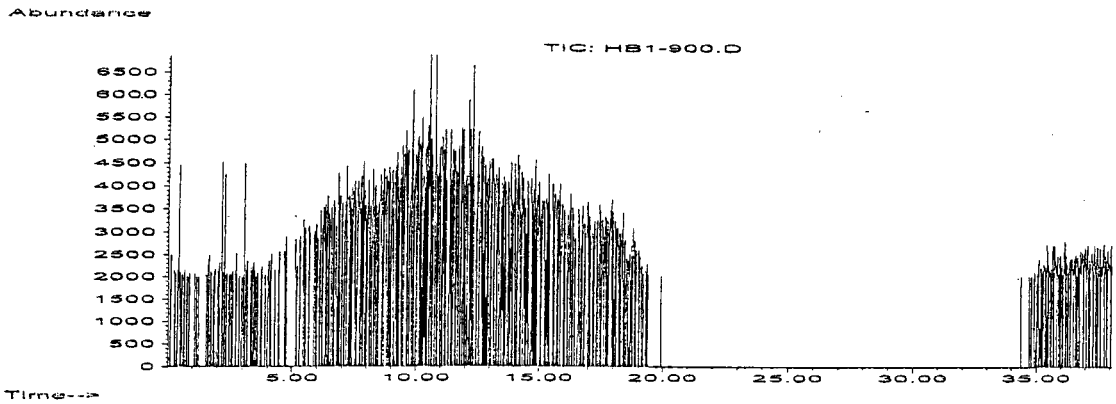

Figure 5.3.2. In-line GC/MS Ion Chromatogram for Heated Blank at 900°C

5.3.2. Off-line GC/MS Analysis

A 0.5 L Tedlar bag (SKC, Inc.) was used to collect the off-gas. The samples were analyzed within 15 minutes after collection. The flow profile was identical to the in-line GC/MS analysis and PUF collection except the last time period, which was not necessary for Tedlar bag analysis. HP5890A/5970B series GC/MS with SPEL-Q PLOT (Porous Layer Open Tubular) column (30 m length, 0.53 mm i.d., Supelco, Inc.) was used for the analyses. The off-line GC/MS was operated in the constant flow mode with 28 ml/min split flow. The MS was auto-tuned with perfluorotributylamine (PFTBA) and operated at an electron multiplier setting of 1600 in the scanning mode sweeping a mass range from 35 to 550 m/z. The Tedlar bags were heated to ca. 50 – 60°C to minimize condensation on the bag surfaces. 1 ml sample volumes were injected using a gas-tight syringe (Hamilton Co.). Figure 5.3.3 and 5.3.4 show total ion chromatograms for the heated blank at 600 and 900°C, respectively. Large peaks associated with air were observed at 0.65 and 0.75 minute (argon and carbon dioxide, respectively). There was no other peaks observed, which indicates the lack of any measurable contamination.

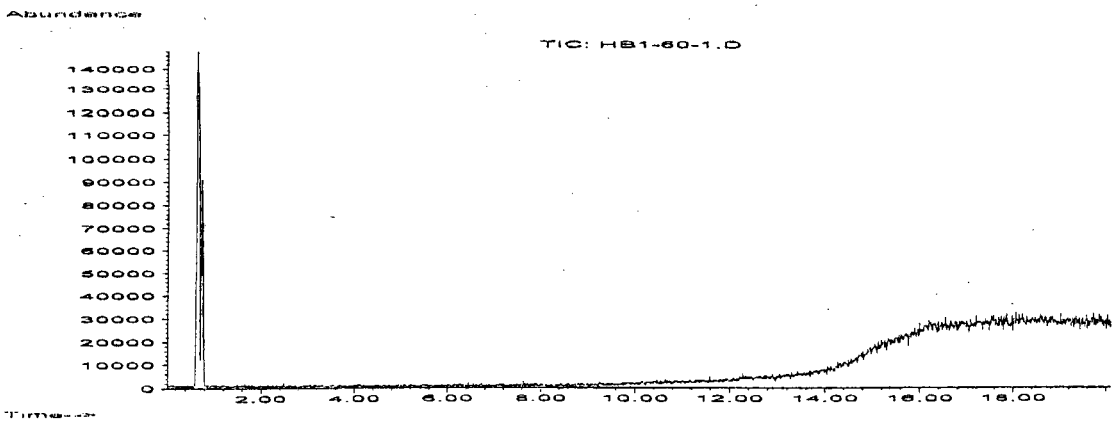

Figure 5.3.3. Off-line GC/MS Ion Chromatogram for Heated Blank at 600°C

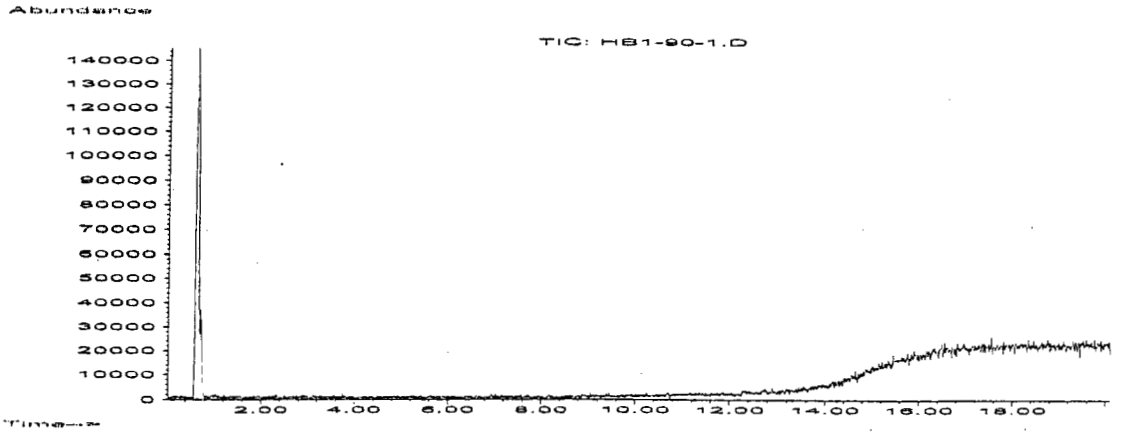

Figure 5.3.4. Off-line GC/MS Ion Chromatogram for Heated Blank at 900°C

5.3.3 Reactor/Transfer Line Extraction and LC-MS Analysis

Following PUF sample collection and in- and off-line GC/MS analysis at 900°C, extraction of the reactor/transfer line tubing was performed. The reactor was cut in half prior to the extraction. The second half of the reactor and the transfer lines between the reactor and switching valve 1 were extracted. Further details regarding the extraction procedure are presented in the phase III test protocol. The extractions were performed twice using 5.5 ml of methanol ((Aldrich, HPLC grade). The extracts were analyzed for PFBS, PFOS at 3M Environmental Laboratory. Table 5.3.3 shows the analytical results. A very small amount of PFOS, 0.08 μg, was found in the reactor/transfer line extract in the first heated blank combustion test. The amount found was equal to 0.016% of the maximum amount that could have passed through the system as PFOS or that could have been formed from any of the fluorochemical product at levels added in the combustion tests. The amount of PFOS extracted in the second heated blank combustion test was below detection limits.

Table 5.3.3. Methanol Extraction Results for Heated Blank Analysis

PFOS (pg/μl)	PFOS(μg)	PFBS(pg/μl)	PFBS(μg)		
14.9	0.10	<10.1	<0.065	<4.96	<0.028

Table 5.3.4 shows the analytical results for the two PUF sample collections. No cross contamination was detected.

Table 5.3.4. PUF Extraction Results for Heated Blank Analysis

Temp (°C)	PFOS(pg/μl)	PFOS(μg)	PFBS(pg/μl)	PFBS(μg)		
600	<10.0	<0.25	<10.1	<0.23	<4.96	<0.10
900	<10.0	<0.25	<10.1	<0.23	<4.96	<0.10

5.4. Combustion Tests of Seven Selected Compounds

Combustion product analyses were performed for seven compounds, FC-1395, FC-807A, , $C_4F_9SO_3^-K^+$ (PFBS) and $C_8F_{17}SO_3^-K^+$ (PFOS). Four distinct analyses were conducted. Two GC/MS analyses were conducted at UDRI: in-line

GC/MS analysis and off-line GC/MS analysis using Tedlar bags. The chemical extractions of the reactor transfer lines were performed at UDRI. The PUF cartridges were extracted at the 3M Environmental Lab. The experimental setup, reactor/transfer-line configuration, and experimental procedure followed the Phase III test protocol. The GC/MS operating conditions for the in-line and off-line analyses were the same as those used for heated blank analyses described in Section 5.3.

In these combustion tests, the samples were first volatilized in a pyroprobe chamber. This chamber is considered analogous to the primary combustion chamber in an incinerator. The gases or air-entrained particulate matter then passed through transfer tubing, a heated tubular reactor, and additional transfer tubing and a valve to PUF cartridges. The heated reactor is considered roughly analogous to a secondary combustion chamber or afterburner in a full-scale incinerator.

5.4.1. Combustion Test

Table 5.4.1.1 shows the net amount of sample gasified for the combustion tests. The sample probe was weighed before and after the combustion tests.

Table 5.4.1.1. Net Amount of Gasified Sample for Combustion Test

Temperature (°C)	Usage	Loaded (mg)	Remained (mg)	Net Amount of Gasified Sample (mg)
600	PUF[a]	2.03	0.02	2.01
	TB[b]	2.11	0.01	2.10
900	PUF	2.22	0.14	2.08
	TB	2.15	0.27	1.88

[a] In-line GC/MS analysis and off-gas collection using PUF. [b] Off-line GC/MS analysis using Tedlar Bag.

Table 5.4.1.2 and Table 5.4.1.3 show flow rate profiles used for combustion tests at 600 and 900°C, respectively. Identical combustion conditions were repeated for PUF collection, in-line GC/MS analysis, and off-line GC/MS analysis for each temperature. The first total volume (3rd row from the bottom) is the summation of all flow steps. A flow of 1 ml/min was always supplied to the in-line GC/MS system. Therefore, the volume passed through the PUF cartridge can be calculated by subtraction of the volume to the in-line GC/MS system from the total volume passed through the reactor as shown in the 2nd row from the bottom:

45.31 ml – [1 ml/min. (269 – 25) sec.] / [60 sec./min.] = 41.24 ml

To calculate the total amount of SO_2 recovered using the off-line GC/MS system, the volume supplied to the in-line GC/MS system also needs to be counted as well as the volume collected by Tedlar bag. This total volume can be calculated by subtraction of the first time step volume (10.97 ml) from the total volume passed through the reactor (45.31 ml) as shown in the last row, since the gas collection was started when the sample was inserted.

At the onset of the experiment, air was flowed through the entire system for 1 minute prior to sample gasification. The pyroprobe/transfer line system was then opened to insert the sample probe within the pyroprobe. At that time, there was no appreciable gas flow through the system.

The sample was then gasified for 40 seconds at 1250°C. During and following this gasification, air flow swept the gasified products from the pyroprobe to the reactor. For the 600°C combustion test with , for example, this air flow rate was 0.47 mL/min at 23°C for 2 min., 24 sec. At 260°C, the temperature of the oven containing the pyroprobe, this air flow would have expanded to sweep the volume of the pyroprobe approximately 2 times. However, the 40 sec. heating to 1250°C to gasify the sample during this flow period would have also forced approximately 1.9 pyroprobe volumes of gas from the pyroprobe to the reactor. During cooling from 1250°C to 260°C following gasification, there was likely also a temporary back air flow into the pyroprobe as the gas pressure inside it dropped. To purge the pyroprobe/transfer line, air flow to the pyroprobe chamber was then increased to the maximum rate and held for 10 seconds. For the 600°C combustion test on for example, this air flow rate was 4.63 mL/min at 23°C. After gas flow to the pyroprobe chamber was increased to the maximum, the total volume of the purging air and helium was 3.8 ml at 23°C, which corresponds to 6.9 ml at 260°C. Since the effective volume of the pyroprobe chamber with the sample probe inserted is 1.5 cm^3 (bottom of page 10 in Phase III protocol), this volume completely flushes the pyroprobe chamber 4.6 times. If one assumes the gas in the pyroprobe is completely mixed, a best-case scenario, this would have carried 99.0% of the gasified from the pyroprobe to the reactor. This purging procedure was applied for all seven combustion tests, and the flow rates profile for each test is given below in tabular form. The head of the GC column was held at the temperature of -60°C during the entire combustion period to concentrate effluent gas that was introduced at 1 ml/min flow rate. The GC/MS temperature programming was started after the final helium purge.

Table 5.4.1.2. Flow Rate Profile for Combustion Test at 600°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)	Total Flow Rate (ml/min)	Volume to Reactor (ml)
0 – 60	10.2	0.47	10.67	10.67
60 – 85[a]	0.00	0.00	0.00	0.00
85 – 229	10.2	0.47	10.67	25.61
229 - 239	10.2	0.47 → 4.63[b]	10.67 → 14.83	2.13
239 – 249	10.2	4.63	14.83	2.47
249 - 269	8.77 (He)[c]	4.53 (He)[d]	13.3	4.43
			Total volume passed through reactor (ml)	45.31[e]
			Total volume passed through PUF (ml)	41.24[f]
			Total volume used for off-line GC/MS SO_2 quantitative analysis (ml)	34.64[g]

[a] System opened due to sample insertion. Assuming no outlet flow. [b] Linear increase (approximate). [c,d] Switched to helium for sweep. [e] Total carrier flow volume that passed through the reactor. [f] Total carrier flow volume that passed through PUFs. [g] Volume used to calculate total amount of SO_2 recovered using off-line GC/MS system.

Table 5.4.1.3. Flow Rate Profile for Combustion at 900°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)	Total Flow Rate (ml/min)	Volume (ml)
0 – 60	7.43	0.36	7.79	7.79
60 – 85[a]	0.00	0.00	0.00	0.00
85 – 265	7.43	0.36	7.79	23.37
265 – 275	7.43	0.36 → 4.63[b]	7.79 → 12.06	1.65
275 - 285	7.43	4.63	12.06	2.01
285 - 305	6.39 (He)[c]	4.53 (He)[d]	10.92	3.64
			Total volume passed through reactor (ml)	38.46[e]
			Total volume passed through PUF (ml)	33.80[f]
			Total volume used for off-line GC/MS SO_2 quantitative analysis (ml)	30.67[g]

[a] System opened due to sample insertion. Assuming no outlet flow. [b] Linear increase (approximate). [c,d] Switched to helium for sweep. [e] Total carrier flow volume that passed through the reactor. [f] Total carrier flow volume that passed through PUFs. [g] Volume used to calculate total amount of SO_2 recovered using off-line GC/MS system.

5.4.1.1. In-line GC/MS Analysis: Figure 5.4.1.1 shows the total ion chromatogram for combustion at 600°C. The first peak at 1.0 min. was identified as pentafluoroethane and the following two peaks were identified as sulfur dioxide. It was often observed for in-line GC/MS analysis that one compound appears as two continuous peaks. These peaks at the beginning of chromatogram were investigated further with off-line GC/MS analysis as described in Section 5.4.1.2. The large peaks at 10 to 11 minutes were identified as benzene, fluorobenzene, difluorobenzene, trifluorobenzene, and their isomers. The largest peak corresponds to benzene. The wide peak which appeared at 12 to 13 min. has a strong mass signal at 85, indicative of tetrafluorosilane. Figure 5.4.1.2 shows original mass spectra (upper spectra) at the largest response time and tetrafluorosilane library spectra (lower spectra). Both have strong m/z = 85 and m/z = 55 signals. The original mass spectra do not contain m/z = 41 since the experimental scanning range was from 45 to 550 m/z. Tetrafluorosilane would be formed in the pyroprobe chamber during the sample gasification at 1250°C and not destroyed in the reactor at 600°C. The peaks following tetrafluorosilane were identified as styrene at 15.5 min., benzaldehyde at 16.4 min., benzonitrile at 16.85 min., phenol at 16.93 min., and naphthalene at 20.2 min. No significant peaks were observed for molecules heavier than naphthalene. This suggests that molecular growth (free radical reactions leading to the formation of larger molecular weight compounds) does not occur for combustion at 600°C. We have previously shown that larger multi-ring polycyclic aromatic hydrocarbons (PAH) and halogenated PAH can be detected with this combustion system in tandem with GC/MS analysis (Taylor and Lenoir, 2001; Sidhu et al., 2001).

Figure 5.4.1.3 shows the total ion chromatogram for combustion at 900°C. A similar chromatogram was obtained. The first peak at 0.5 to 1.0 min. was not clearly identified. The following peak at 2.0 min. corresponds to sulfur dioxide. The large peaks at 10 to 11 minutes are benzene, fluorobenzene, difluorobenzene, trifluorobenzene, and their isomers. The largest peak corresponds to benzene. The wide peak appeared at 12.5 to 15 minutes has strong spectrum of 85, suggesting tetrafluorosilane. The retention time and peak width of tetrafluorosilane differed from the 600°C combustion results. While the reasons for this are not completely clear, this is potentially due in part to differences in the time duration of the cryofocusing of the organic products and differences in the column head pressure because of the flow rate differences at the

last flow step. This phenomena was observed for all in-line GC/MS total ion chromatograms. The peaks after tetrafluorosilane include styrene at 15.6 min., benzonitrile at 17.5 min., and naphthalene at 20.25 min. Fewer aromatics were formed at 900°C than at 600°C. This suggests that further molecular growth did not occur for combustion at 900°C. Sulfur recovery rate as sulfur dioxide is reported in Section 5.7 of the experimental results.

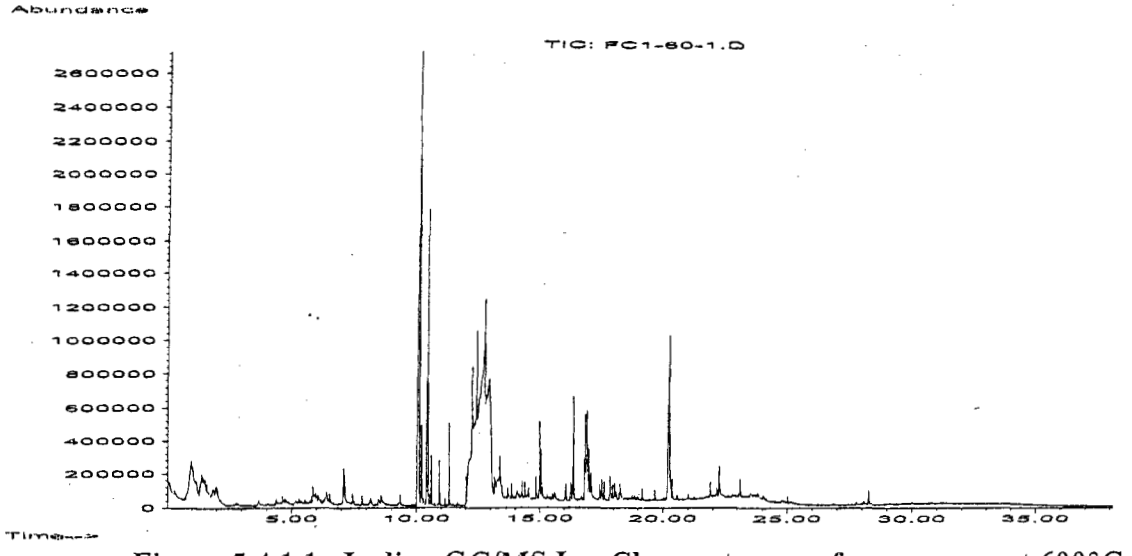

Figure 5.4.1.1. In-line GC/MS Ion Chromatogram for at 600°C

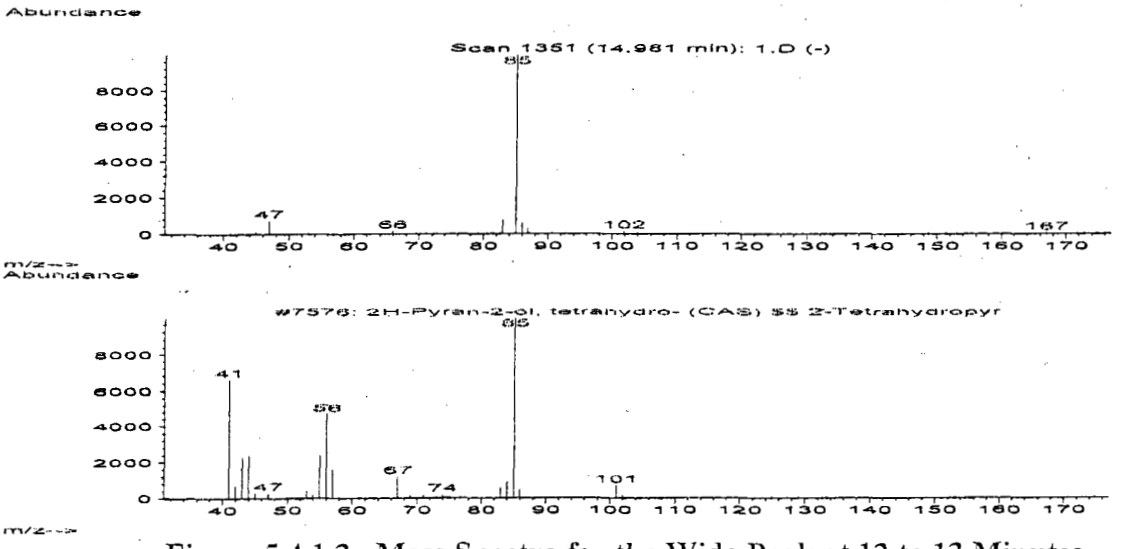

Figure 5.4.1.2. Mass Spectra for the Wide Peak at 12 to 13 Minutes

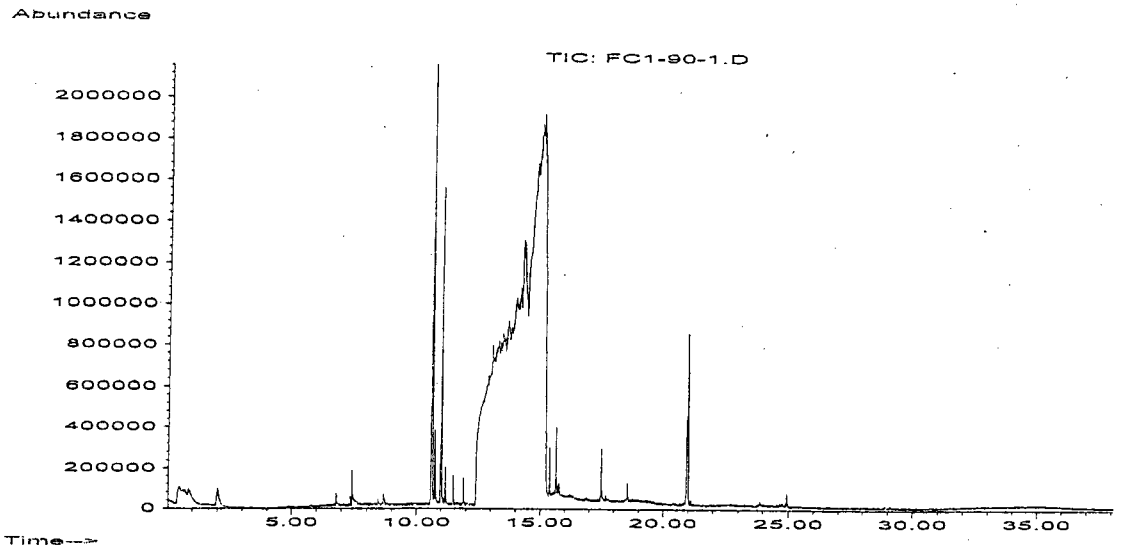

Figure 5.4.1.3. In-line GC/MS Ion Chromatogram for at 900°C

5.4.1.2. Off-line GC/MS Analysis: Figure 5.4.1.4 shows the total ion chromatogram for off-line GC/MS analyses for combustion at 600°C. The largest peak at the beginning is associated with air (see extracted ion analysis, section 5.9) followed by 1,1-difluoroethene at 1.0 min., pentafluoroethane at 1.7 min., sulfur dioxide at 3 min. The wide peak at 4.7 to 5.4 min could not be clearly identified. The three peaks around 10 min. were identified as benzene, difluorobenzene (isomer unclear), and fluorobenzene, in this order. Figure 5.4.1.5 shows the total ion chromatogram for off-line GC/MS analyses for combustion at 900°C. The first 2 peaks before 1 min. are associated with air followed by sulfur dioxide at 3.0 min. No other significant peaks were observed for combustion at 900°C.

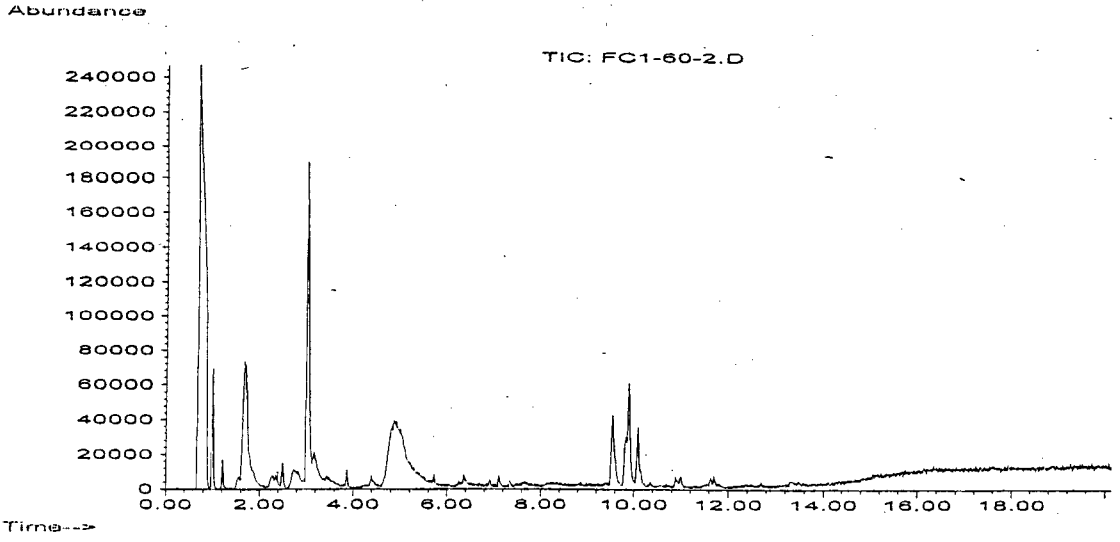

Figure 5.4.1.4. Off-line GC/MS Ion Chromatogram for at 600°C

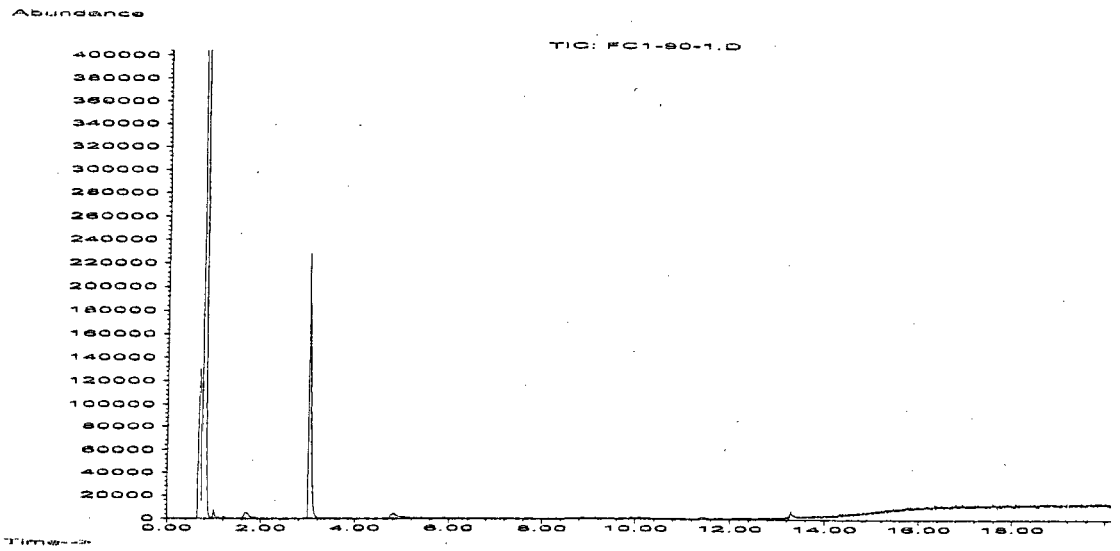

Figure 5.4.1.5. Off-line GC/MS Ion Chromatogram for at 900°C

5.4.1.3. LC-MS Analysis of Extracts: Table 5.4.1.4 shows the analytical results of the reactor/ transfer line extractions. No detectable amount of PFOS, PFBS, was found.

Table 5.4.1.4. Methanol Extraction Results for Combustion Test

Extraction	PFOS(pg/μl)	PFOS(μg)	PFBS(pg/μl)	PFBS(μg)		
1st	<5.00	<0.035	<5.05	<0.032	<4.96	<0.028
2nd	<5.00	<0.035	<5.05	<0.032	<4.96	<0.028

5.4.1.4. LC-MS Analysis of PUFs: Table 5.4.1.5 shows the analytical results for the PUF sampling cartridges. No detectable amount of PFOS, PFBS, was found.

Table 5.4.1.5. PUF Extraction Results for Combustion Test

Temp (°C)	Media	PFOS (pg/μl)	PFOS (μg)	PFBS (pg/μl)	PFBS (μg)	(pg/μg)	(μl)
600	PUF (1st)	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10
	PUF (2nd)	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10
900	PUF (1st)	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10
	PUF (2nd)	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10

5.4.2. Combustion Test

Table 5.4.2.1 shows net amount of sample gasified for the combustion tests. The sample probe was weighed before and after the combustion tests.

Table 5.4.2.1. Net Amount of Gasified Sample for Combustion Test

Temperature (°C)	Usage	Loaded (mg)	Remained (mg)	Net Amount of Gasified Sample (mg)
600	PUF[a]	2.85	0.05	2.80
	TB[b]	2.80	0.02	2.78
900	PUF	2.82	0.06	2.76
	TB	2.98	0.04	2.94

[a] In-line GC/MS analysis and off-gas collection using PUF. [b] Off-line GC/MS analysis using Tedlar Bag.

Table 5.4.4.2 and 5.4.2.3 shows flow rate profiles used for combustion tests at 600 and 900°C, respectively. The detailed explanation for each value can be found in section 5.4.1

Table 5.4.2.2. Flow Rate Profile for Combustion Test at 600°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)	Total Flow Rate (ml/min)	Volume (ml)
0 – 60	11.9	0.29	12.19	12.19
60 – 85[a]	11.9	0.00	0.00	0.00
85 – 301	11.9	0.29	12.19	43.88
301 – 311	11.9	0.29 → 4.63[b]	12.19 → 16.53	2.39
311 – 321	11.9	4.63	16.53	2.75
321 - 341	10.2 (He)[c]	4.53 (He)[d]	14.73	4.91
			Total volume passed through reactor (ml)	66.12[e]
			Total volume passed through PUF (ml)	60.87[f]
			Total volume used for off-line GC/MS SO_2 quantitative analysis (ml)	53.93[g]

[a] System opened due to sample insertion. Assuming no outlet flow. [b] Linear increase (approximate). [c,d] Switched to helium for sweep. [e] Total carrier flow volume that passed through the reactor. [f] Total carrier flow volume that passed through PUFs. [g] Volume used to calculate total amount of SO_2 recovered using off-line GC/MS system.

Table 5.4.2.3. Flow Rate Profile for Combustion Test at 900°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)	Total Flow Rate (ml/min)	Volume (ml)
0 – 60	9.11	0.21	9.32	9.32
60 – 85[a]	0.00	0.00	0.00	0.00
85 – 373	9.11	0.21	9.32	44.74
373 – 383	9.11	0.21 → 4.63[b]	9.32 → 13.74	1.92
383 – 393	9.11	4.63	13.74	2.29
393 - 413	7.83 (He)[c]	4.53 (He)[d]	12.36	4.12
			Total volume passed through reactor (ml)	62.39[e]
			Total volume passed through PUF (ml)	55.92[f]
			Total volume used for off-line GC/MS SO_2 quantitative analysis (ml)	53.07[g]

[a] System opened due to sample insertion. Assuming no outlet flow. [b] Linear increase (approximate). [c,d] Switched to helium for sweep. [e] Total carrier flow volume that passed through the reactor. [f] Total carrier flow volume that passed through PUFs. [g] Volume used to calculate total amount of SO_2 recovered using off-line GC/MS system.

5.4.2.1. In-line GC/MS Analysis: Figure 5.4.2.1 shows the total ion chromatogram for combustion at 600°C. The first peak at 6.5 min. was identified as carbon disulfide and the largest peak at 10.4 min. was identified as benzene followed by fluorobenzene at 10.7 min. The

wide peak appearing at 12.5 to 15 minutes corresponds to tetrafluorosilane. The peaks after tetrafluorosilane include styrene at 15.3 min., benzaldehyde at 16.7 min., benzonitrile at 17.2 min., phenol at 17.3 min., and naphthalene at 20.6 min. Figure 5.4.2.2 shows total ion chromatogram for combustion at 900°C. A similar chromatogram was obtained. The first peak at 6.6 min. was identified as carbon disulfide and the largest peak at 10.5 min. was identified as benzene followed by fluorobenzene at 10.8 min. The peak at 12.8 min. was identified as toluene. The wide peak appearing at 13.3 to 14.2 minutes corresponds to tetrafluorosilane. The peaks after tetrafluorosilane include ethynylbenzene at 15.2 min., styrene at 15.4 min., indene at 18.3 min., naphthalene at 20.8 min., and acenaphthalene at 24.7 min.

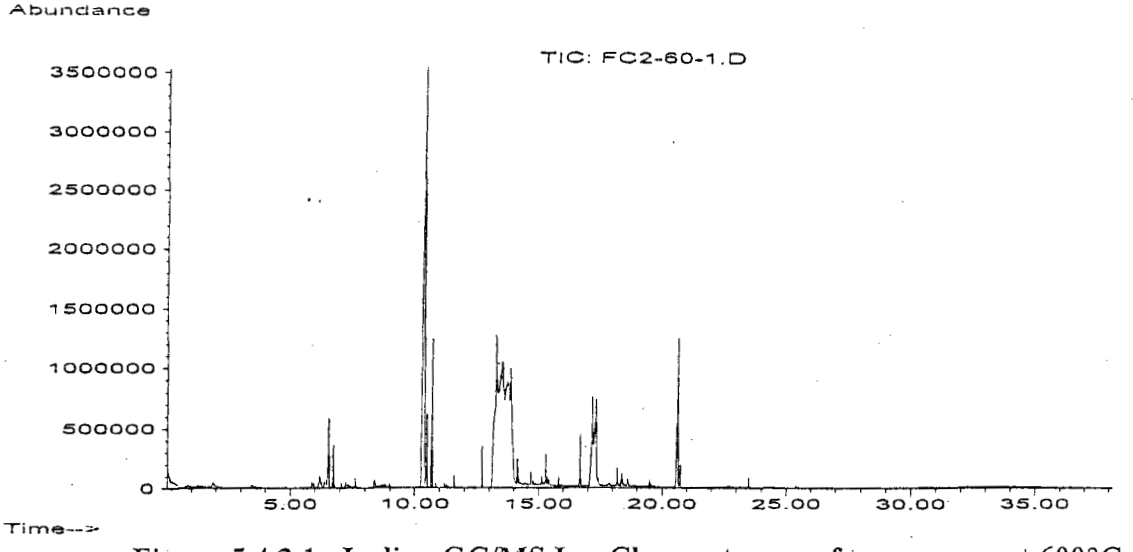

Figure 5.4.2.1. In-line GC/MS Ion Chromatogram for at 600°C

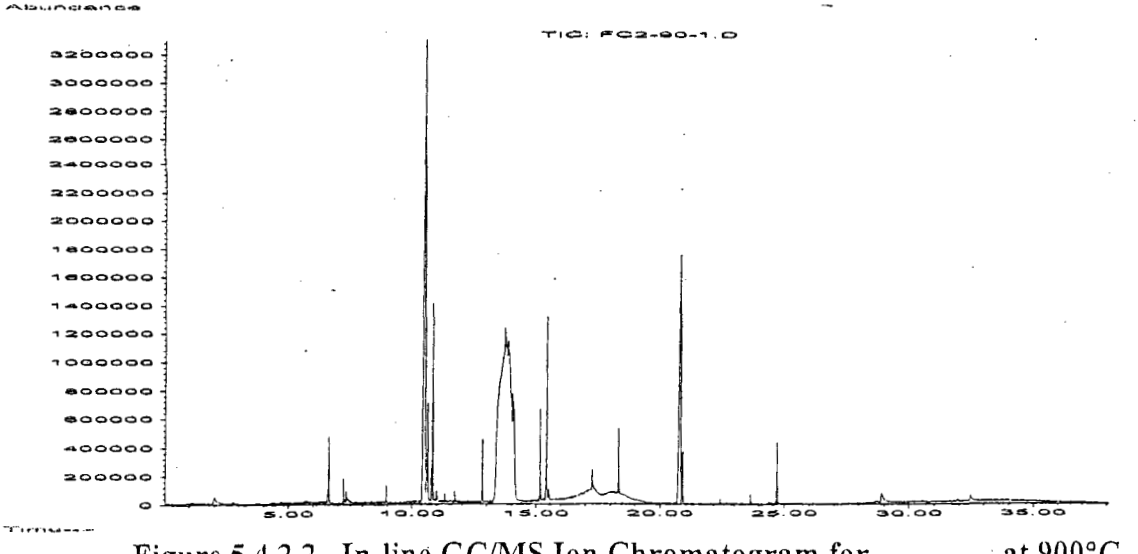

Figure 5.4.2.2. In-line GC/MS Ion Chromatogram for at 900°C

5.4.2.2. Off-line GC/MS Analysis: Figure 5.4.2.3 shows the total ion chromatogram for off-line GC/MS analyses for combustion at 600°C. The large peak at the beginning is associated with air. The major peaks found in this chromatogram were sulfur dioxide at 3.0 min.,

carbon disulfide at 6.9 min., benzene at 9.9 min., and fluorobenzene at 10.1 min. Figure 5.4.2.4 shows ion chromatogram for off-line GC/MS analyses for combustion at 900°C. A similar chromatogram was obtained for 900°C combustion, but both sulfur dioxide and benzene peaks are slightly smaller than for the 600°C combustion.

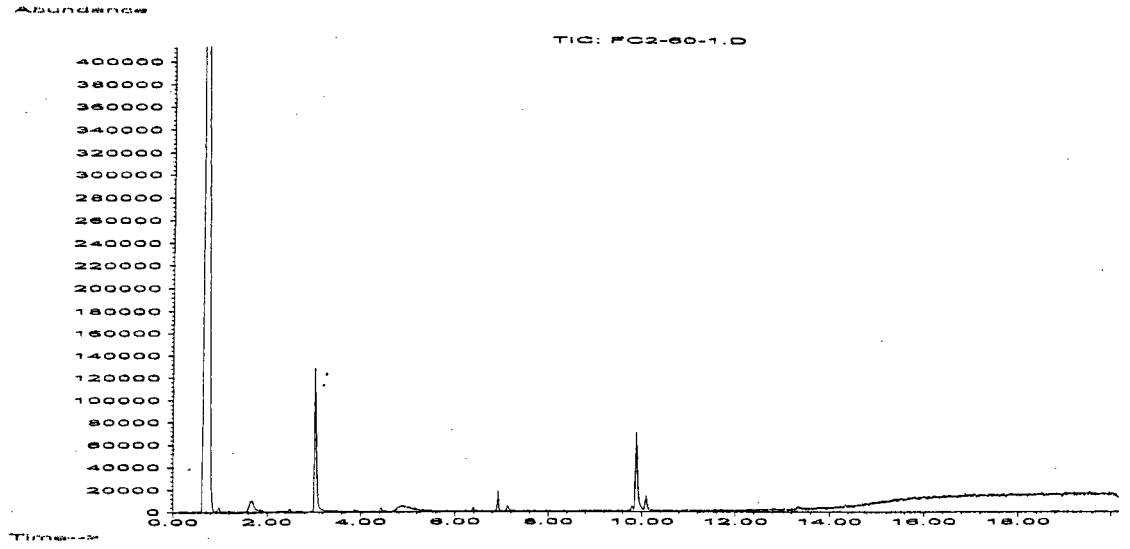

Figure 5.4.2.3. Off-line GC/MS Ion Chromatogram for at 600°C

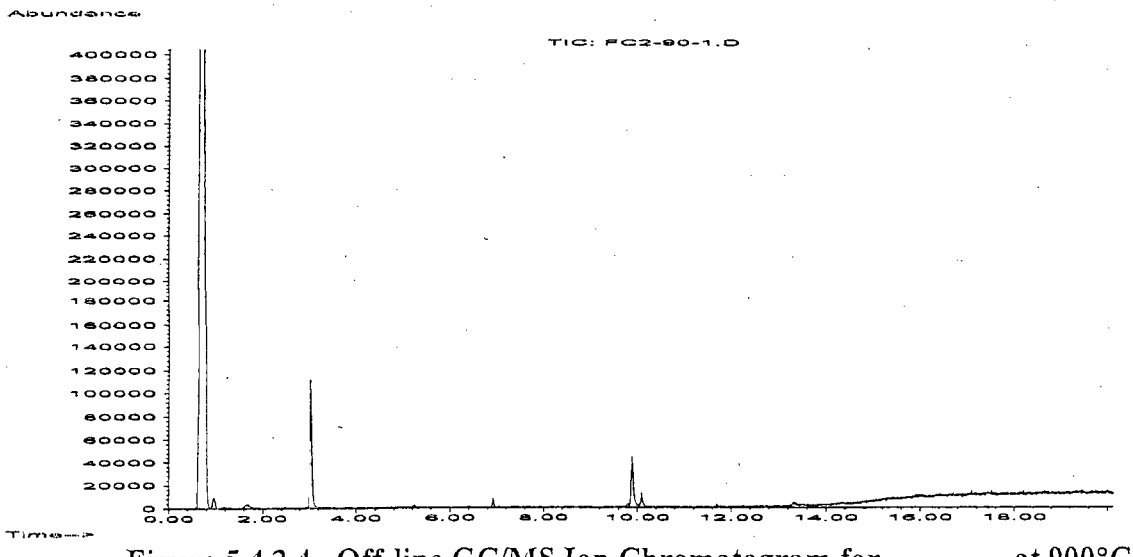

Figure 5.4.2.4. Off-line GC/MS Ion Chromatogram for at 900°C

5.4.2.3. LC-MS Analysis of Extracts: Table 5.4.2.4 shows the analytical results of the reactor/ transfer line extractions. No detectable amount of PFOS, PFBS, was found.

Table 5.4.2.4. Methanol Extraction Results for Combustion Test

Extraction	PFOS(pg/µl)	PFOS(µg)	PFBS(pg/µl)	PFBS(µg)		
1st	<5.00	<0.035	<5.05	<0.032	<4.96	<0.028
2nd	<5.00	<0.035	<5.05	<0.032	<4.96	<0.028

5.4.2.4. LC-MS Analysis of PUFs: Table 5.4.2.5 shows the analytical results for the PUF sampling cartridges. No detectable amount of PFOS, PFBS, was found.

Table 5.4.2.5. PUF Extraction Results for FC-4430 Combustion Test

Temp (°C)	Media	PFOS (pg/μl)	PFOS (μg)	PFBS (pg/μl)	PFBS (μg)	(pg/μg)	(μl)
600	PUF (1^{st})	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10
	PUF (2^{nd})	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10
900	PUF (1^{st})	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10
	PUF (2^{nd})	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10

5.4.3. FC-1395 Combustion Test

Table 5.4.3.1 shows net amount of sample gasified for FC-1395 combustion tests. The sample probe was weighed before and after the combustion tests.

Table 5.4.3.1. Net Amount of Gasified Sample for FC-1395 Combustion Test

Temperature (°C)	Usage	Loaded Mass (mg)	Dried Mass[c] (mg)	Remaining (mg)	Net Amount of Gasified Sample (mg)
600	PUF[a]	2.14	0.56	0.04	0.52
	TB[b]	2.22	0.58	0.06	0.52
900	PUF	2.20	0.57	0.02	0.55
	TB	2.23	0.58	0.15	0.43

[a] In-line GC/MS analysis and off-gas collection using PUF. [b] Off-line GC/MS analysis using Tedlar Bag.
[c] Calculated based on the water contents (74%).

Table 5.4.3.2 and 5.4.3.3 shows flow rate profiles used for FC-1395 combustion tests at 600 and 900°C, respectively. The detailed explanation for each value can be found in section 5.4.1.

Table 5.4.3.2. Flow Rate Profile for FC-1395 Combustion Test at 600°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)		Total Flow Rate (ml/min)	Volume (ml)
	Air	Air	CH_4		
0 – 60	9.53	0.85	0.16	10.54	10.54
60 – 85[a]	0.00	0.00	0.00	0.00	0.00
85 – 157	9.53	0.85	0.16	10.54	12.65
157 - 167	9.53	0.85 → 4.63[b]	0.16	10.54 → 14.32	2.07
167 - 177	9.53	4.63	0.16	14.32	2.39
177 - 197	8.20 (He)[c]	4.53 (He)[d]	0	12.73	4.24
				Total volume passed through reactor (ml)	31.89[e]
				Total volume passed through PUF (ml)	29.02[f]
				Total volume used for off-line GC/MS SO_2 quantitative analysis (ml)	21.35[g]

[a] System opened due to sample insertion. Assuming no outlet flow. [b] Linear increase (approximate). [c,d] Switched to helium for sweep. [e] Total carrier flow volume that passed through the reactor. [f] Total carrier flow volume that passed through PUFs. [g] Volume used to calculate total amount of SO_2 recovered using off-line GC/MS system.

Table 5.4.3.3. Flow Rate Profile for FC-1395 Combustion Test at 900°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)		Total Flow Rate (ml/min)	Volume (ml)
	Air	Air	CH_4		
0 – 60	7.14	0.63	0.12	7.89	7.89
60 – 85[a]	0.00	0.00	0.00	0.00	0.00
85 – 179	7.14	0.63	0.12	7.89	12.36
179 – 189	7.14	0.63 → 4.63[b]	0.12	7.89 → 11.89	1.65
189 – 199	7.14	4.63	0.12	11.89	1.98
199 - 219	6.14 (He)[c]	4.53 (He)[d]	0	10.67	3.56
				Total volume passed through reactor (ml)	27.44[e]
				Total volume passed through PUF (ml)	24.20[f]
				Total volume used for off-line GC/MS SO_2 quantitative analysis (ml)	19.55[g]

[a] System opened due to sample insertion. Assuming no outlet flow. [b] Linear increase (approximate). [c,d] Switched to helium for sweep. [e] Total carrier flow volume that passed through the reactor. [f] Total carrier flow volume that passed through PUFs. [g] Volume used to calculate total amount of SO_2 recovered using off-line GC/MS system.

5.4.3.1. In-line GC/MS Analysis: Figure 5.4.3.1 shows the total ion chromatogram for FC-1395 combustion at 600°C. The first peak at 0.4 to 1.0 min. was not clearly identified. The second peak at 1.7 to 2.4 corresponds to sulfur dioxide. The peak at 7.1 min. was identified as carbon disulfide and the largest peak at 10 minutes was identified as benzene followed by fluorobenzene at 11.1 min. The wide peak appeared at 10 to 13 minutes corresponds to tetrafluorosilane. The peaks after tetrafluorosilane include benzonitrile at 17.7 min. and naphthalene at 21.1 min. Figure 5.4.3.2 shows the total ion chromatogram for FC-1395 combustion at 900°C. The first peak at 2.2 min. was identified as sulfur dioxide and the peak at 11 min. was identified as benzene. The sharp peak at 14.2 minutes and the subsequent wide peak both show a strong 85 signal that is attributed to tetrafluorosilane.

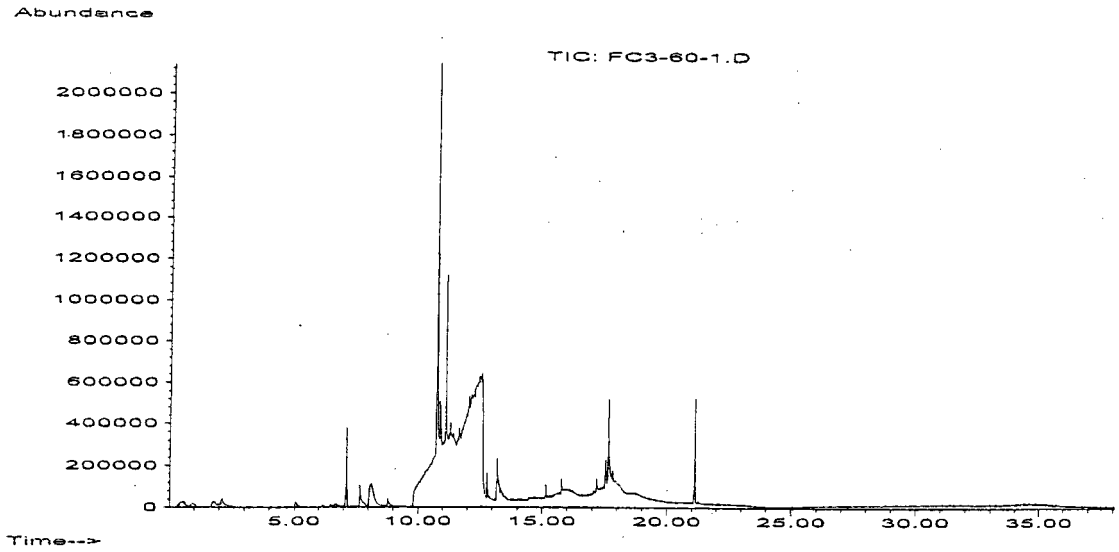

Figure 5.4.3.1. In-line GC/MS Ion Chromatogram for FC-1395 at 600°C

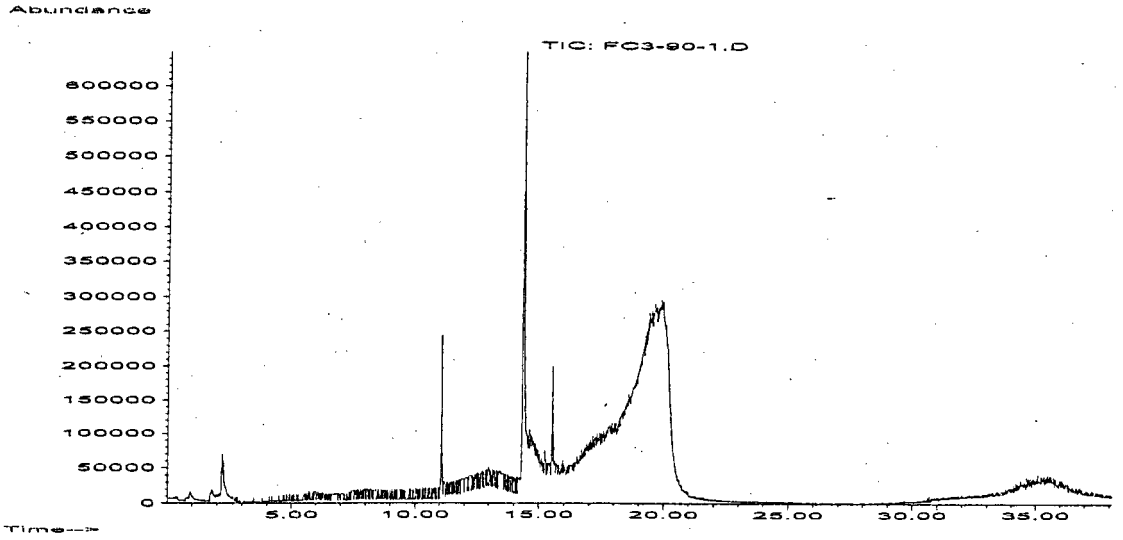

Figure 5.4.3.2. In-line GC/MS Ion Chromatogram for FC-1395 at 900°C

5.4.3.2. Off-line GC/MS Analysis: Figure 5.4.3.3 shows the total ion chromatogram for off-line GC/MS analyses for FC-1395 combustion at 600°C. The large peak at the beginning is associated with air. The next peak at 0.9 min. was identified as 1,2-difluoroethene followed by sulfur dioxide at 3 min., difluorodimethylsilane at 4.8 min., benzene at 9.9 min. and fluorobenzene at 10.1 min. Difluorodimethylsilane also is likely produced during the gasification process. Figure 5.4.3.4 shows the total ion chromatogram for off-line GC/MS analyses for FC-1395 combustion at 900°C. The largest peak is associated with air. Sulfur dioxide at 3 min. was the only identifiable product.

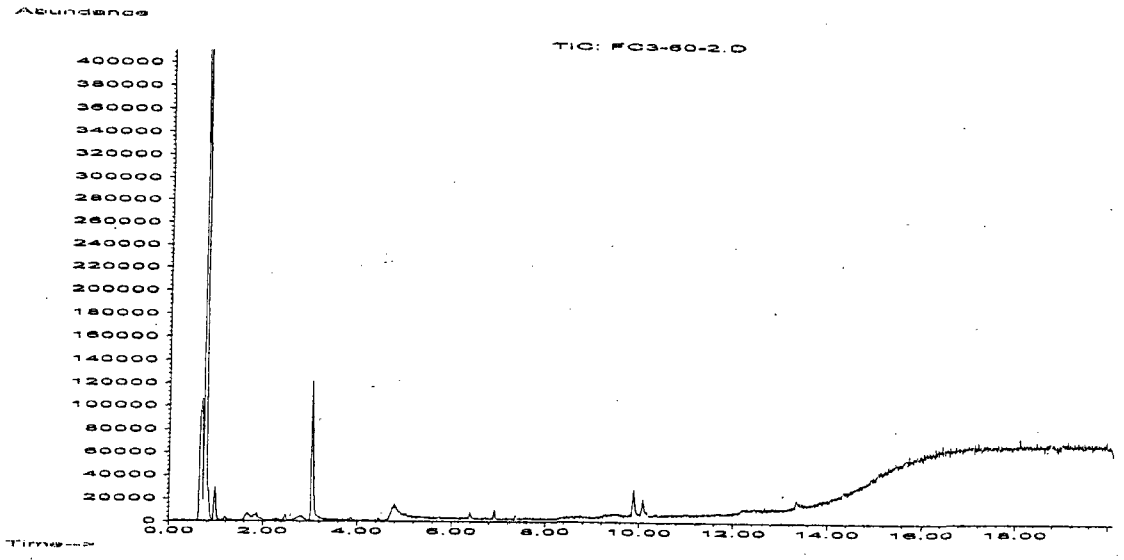

Figure 5.4.3.3. Off-line GC/MS Ion Chromatogram for FC-1395 at 600°C

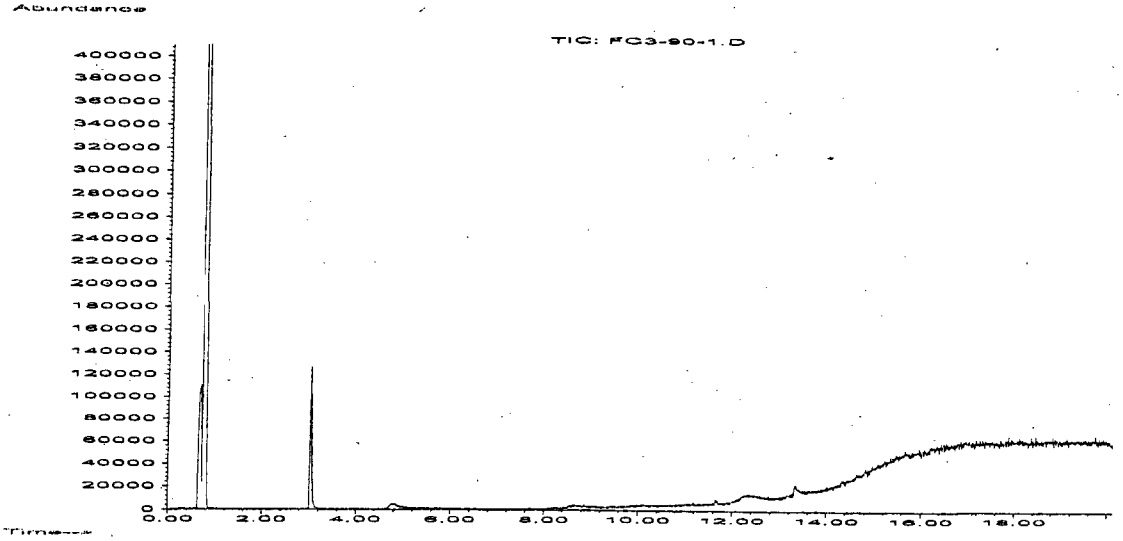

Figure 5.4.3.4. Off-line GC/MS Ion Chromatogram for FC-1395 at 900°C

5.4.3.3. LC-MS Analysis of Extracts: Table 5.4.3.4 shows the analytical results of the reactor/ transfer line extractions. No detectable amount of PFOS, PFBS, was found.

Table 5.4.3.4. Methanol Extraction Results for FC-1395 Combustion Test

Extraction	PFOS(pg/µl)	PFOS(µg)	PFBS(pg/µl)	PFBS(µg)		
1st	<5.00	<0.035	<5.05	<0.032	<4.96	<0.028
2nd	<5.00	<0.035	<5.05	<0.032	<4.96	<0.028

5.4.3.4. LC-MS Analysis of PUF: Table 5.4.3.5 shows the analytical results for the PUF sampling cartridges. No detectable amount of PFOS, PFBS, was found.

Table 5.4.3.5. PUF Extraction Results for FC-1395 Combustion Test

Temp (°C)	Media	PFOS (pg/μl)	PFOS (μg)	PFBS (pg/μl)	PFBS (μg)	(pg/μg)	(μl)
600	PUF (1st)	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10
	PUF (2nd)	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10
900	PUF (1st)	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10
	PUF (2nd)	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10

5.4.4. FC-807A Combustion Test

Table 5.4.4.1 shows net amount of sample gasified for FC-807A combustion tests. The sample probe was weighed before and after the combustion tests.

Table 5.4.4.1. Net Amount of Gasified Sample for FC-807A Combustion Test

Temperature (°C)	Usage	Loaded Mass (mg)	Dried Mass[c] (mg)	Remaining (mg)	Net Amount of Gasified Sample (mg)
600	PUF[a]	2.68	0.59	0.00	0.59
	TB[b]	2.68	0.59	0.00	0.59
900	PUF	2.43	0.53	0.08	0.45
	TB	2.55	0.55	0.02	0.53

[a] In-line GC/MS analysis and off-gas collection using PUF. [b] Off-line GC/MS analysis using Tedlar Bag.
[c] Calculated based on the water contents (78%).

Tables 5.4.4.2, 5.4.4.3, and 5.4.4.4 show the flow rate profiles used for FC-807A combustion tests at 600 and 900°C, and the blank test between 600 and 900°C, respectively. The detailed explanation for each value can be found in section 5.4.1. PUF samples were collected from the blank runs between the 600° and 900°C test runs. The unheated valve/transfer line tubing downstream of the reactor/transfer line tubing was also extracted after the combustion test at 600°C. The purpose of these analyses was to measure the carryover between the tests on a single fluorocarbon product done at 600 and 900°C.

Table 5.4.4.2. Flow Rate Profile for FC-807A Combustion Test at 600°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)		Total Flow Rate (ml/min)	Volume (ml)
	Air	Air	CH_4		
0 – 60	9.70	0.84	0.15	10.69	10.69
60 – 85[a]	0.00	0.00	0.00	0.00	0.00
85 – 157	9.70	0.84	0.15	10.69	12.83
157 - 167	9.70	0.84 → 4.63[b]	0.15	10.69 → 14.48	2.10
167 - 177	9.70	4.63	0.15	14.48	2.41
177 - 197	8.89 (He)[c]	4.53 (He)[d]	0	13.42	4.47
			Total volume passed through reactor (ml)		32.50[e]
			Total volume passed through PUF (ml)		29.64[f]
			Total volume used for off-line GC/MS SO_2 quantitative analysis (ml)		21.81[g]

[a] System opened due to sample insertion. Assuming no outlet flow. [b] Linear increase (approximate). [c,d] Switched to helium for sweep. [e] Total carrier flow volume that passed through the reactor. [f] Total carrier flow volume that passed through PUFs. [g] Volume used to calculate total amount of SO_2 recovered using off-line GC/MS system.

Table 5.4.4.3. Flow Rate Profile for FC-807A Combustion Test at 900°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)		Total Flow Rate (ml/min)	Volume (ml)
	Air	Air	CH_4		
0 – 60	7.25	0.66	0.12	8.03	8.03
60 – 84[a]	0.00	0.00	0.00	0.00	0.00
84 – 178	7.25	0.66	0.12	8.03	12.58
178 - 188	7.25	0.66 → 4.63[b]	0.12	8.03 → 12.00	1.67
188 - 198	7.25	4.63	0.12	12.00	2.00
198 - 218	6.27 (He)[c]	4.53 (He)[d]	0	10.80	3.60
				Total volume passed through reactor (ml)	27.88[e]
				Total volume passed through PUF (ml)	24.65[f]
				Total volume used for off-line GC/MS SO_2 quantitative analysis (ml)	19.85[g]

[a] System opened due to sample insertion. Assuming no outlet flow. [b] Linear increase (approximate). [c,d] Switched to helium for sweep. [e] Total carrier flow volume that passed through the reactor. [f] Total carrier flow volume that passed through PUFs. [g] Volume used to calculate total amount of SO_2 recovered using off-line GC/MS system.

Table 5.4.4.4. Flow Rate Profile for Blank Analysis between 600 and 900°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)		Total Flow Rate (ml/min)	Volume (ml)
	Air	Air	CH_4		
0 – 120	9.70	0.84	0.00	10.54	21.08
120 – 130	9.70	0.84 → 4.63[a]	0.00	10.54 → 14.33	2.07
130 – 140	9.70	4.63	0.00	14.33	2.39
140 - 160	8.89 (He)[b]	4.53 (He)[c]	0.00	13.42	4.47
				Total Volume (ml)	30.01

[a] Linear increase (approximate). [b,c] Switched to helium for sweep

5.4.4.1. In-line GC/MS Analysis: Figure 5.4.4.1 shows the total ion chromatogram for FC-807A combustion at 600°C. The first peak at 0.6 to 1.3 min. was not clearly identified. The second peak at 1.9 to 2.4 min. was identified as sulfur dioxide. Each compound has two consecutive peaks that have the same mass spectra and it apparently occurs as explained in Section 5.4.1. The peak at 7.1 min. was identified as carbon disulfide. The peak at 8.1 min. which shows strong spectra at m/z = 69 and 51 was not clearly identified. Peaks at 10.3 and 11.1 min. were identified as benzene and fluorobenzene, respectively. The wide peak that appeared at 11.2 to 12.6 min and the subsequent background correspond to tetrafluorosilane. The two major peaks after tetrafluorosilane were not clearly identified. Figure 5.4.4.2 shows the total ion chromatogram for FC-807A combustion at 900°C. The first peak at 2.0 to 2.8 min. corresponds to sulfur dioxide. The largest peak at 15.4 min. and the subsequent high background correspond to tetrafluorosilane.

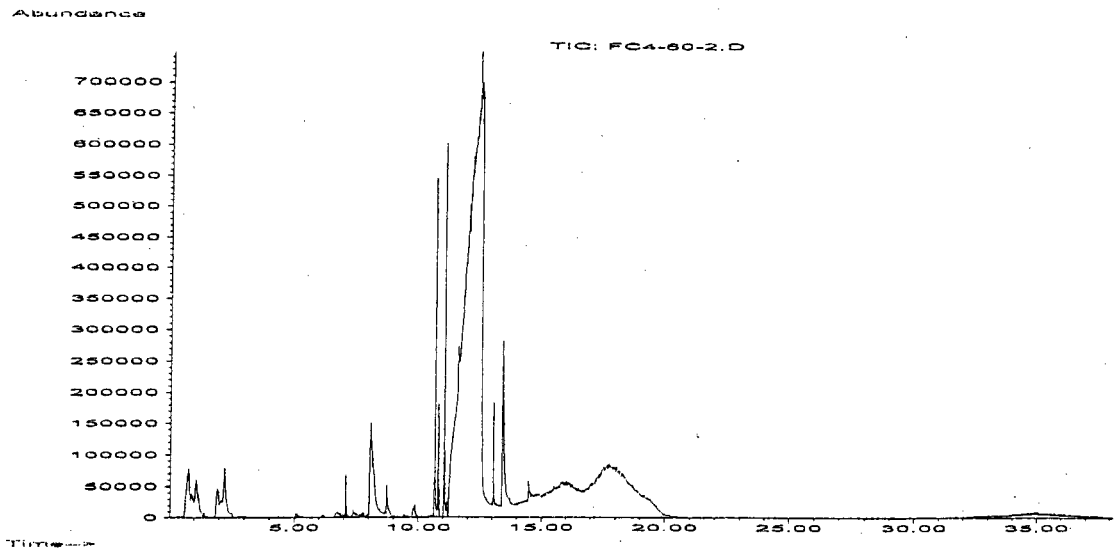

Figure 5.4.4.1. In-line GC/MS Ion Chromatogram for FC-807A at 600°C

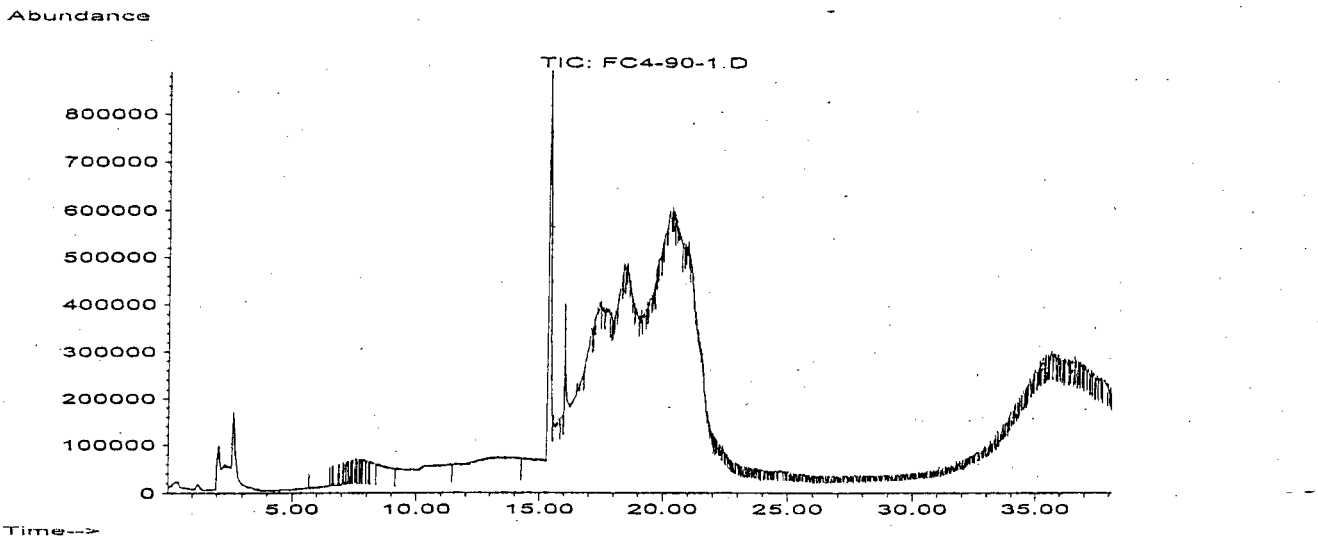

Figure 5.4.4.2. In-line GC/MS Ion Chromatogram for FC-807A at 900°C

5.4.4.2. Off-line GC/MS Analysis: Figure 5.4.4.3 shows the total ion chromatogram for off-line GC/MS analyses for FC-807A combustion at 600°C. The largest peak at the beginning is associated with air. The second peak at 3.0 min. and the third peak at 4.8 min. were identified as sulfur dioxide and difluorodimethylsilane, respectively. There were no further identifiable peaks. Figure 5.4.4.4 shows the total ion chromatogram for off-line GC/MS analyses for FC-807A combustion at 900°C. Similar results were obtained. The largest peak at the beginning is associated with air. The second peak at 3.0 min. and the third peak at 4.8 min. correspond to sulfur dioxide and difluorodimethylsilane, respectively.

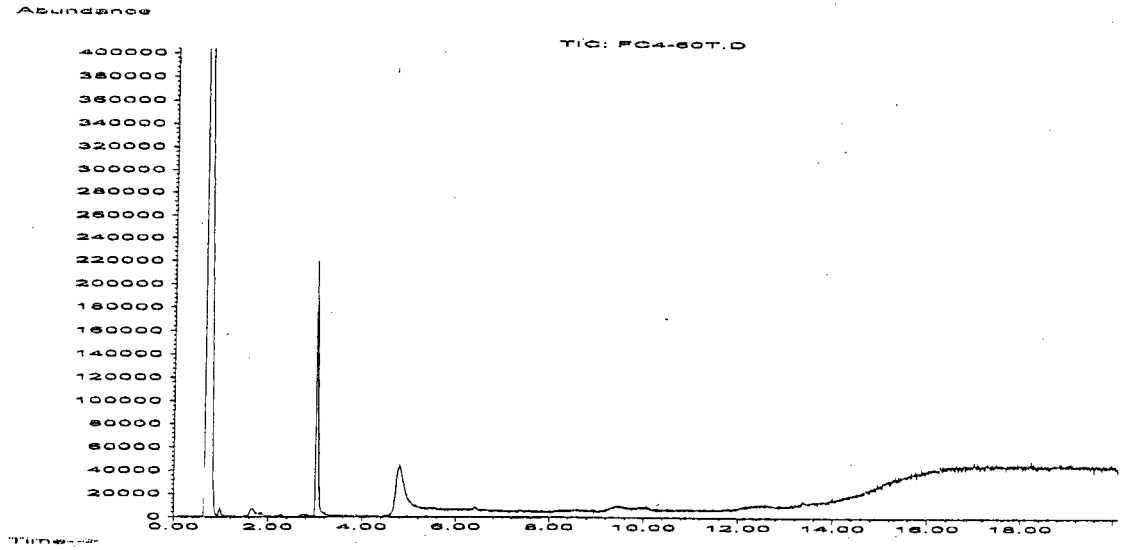

Figure 5.4.4.3. Off-line GC/MS Ion Chromatogram for FC-807A at 600°C

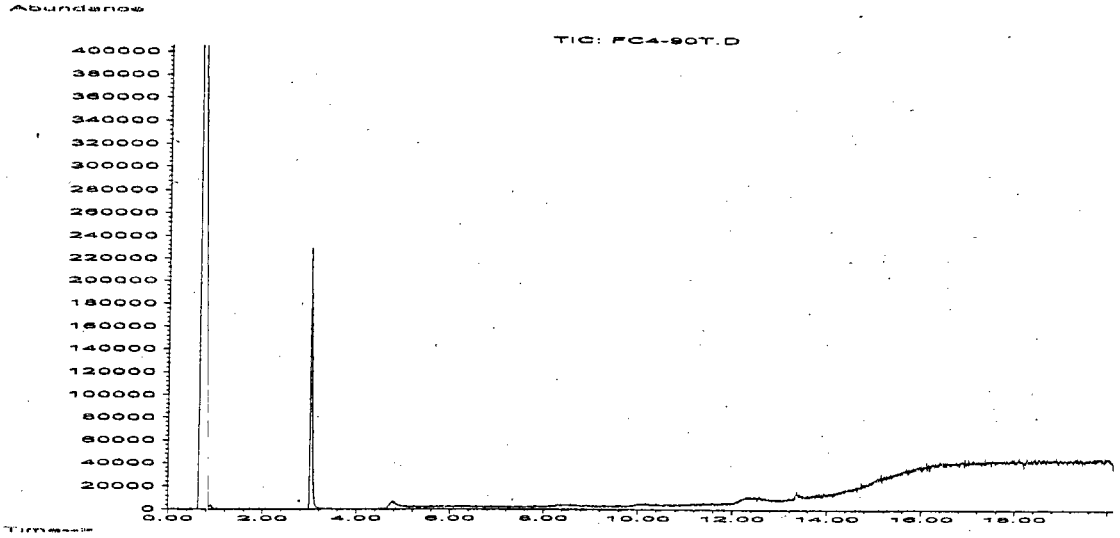

Figure 5.4.4.4. Off-line GC/MS Ion Chromatogram for FC-807A at 900°C

5.4.4.3. LC-MS Analysis of Extracts: Table 5.4.4.5 shows the analytical results of the reactor/transfer line extractions. No detectable amount of PFOS, PFBS, was found.

Table 5.4.4.5. Methanol Extraction Results for FC-807A Combustion Test

Extraction	PFOS(pg/μl)	PFOS(μg)	PFBS(pg/μl)	PFBS(μg)		
1st	<5.00	<0.035	<5.05	<0.032	<4.96	<0.028
2nd	<5.00	<0.035	<5.05	<0.032	<4.96	<0.028

5.4.4.4. LC-MS Analysis of PUF: Table 5.4.4.6 shows the analytical results for the PUF sampling cartridges. No detectable amount of PFOS, PFBS,

Table 5.4.4.6. PUF Extraction Results for FC-807A Combustion Test

Temp (°C)	Media	PFOS (pg/μl)	PFOS (μg)	PFBS (pg/μl)	PFBS (μg)	(pg/μg)	(μl)
600	PUF (1st)	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10
	PUF (2nd)	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10
900	PUF (1st)	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10
	PUF (2nd)	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10

5.4.5. Combustion Test

Table 5.4.5.1 shows the net amount of sample gasified for combustion tests. The sample probe was weighed before and after the combustion tests.

Table 5.4.5.1. Net Amount of Gasified Sample for Combustion Test

Temperature (°C)	Usage	Loaded Mass (mg)	Remaining (mg)	Net Amount of Gasified Sample (mg)
600	PUF[a]	0.55	0.03	0.52
	TB[b]	0.58	0.06	0.52
900	PUF	0.56	0.01	0.55
	TB	0.54	0.00	0.54

[a] In-line GC/MS analysis and off-gas collection using PUF. [b] Off-line GC/MS analysis using Tedlar Bag.

Tables 5.4.5.2, 5.4.5.3, and 5.4.5.4 show flow rate profiles used for combustion tests at 600 and 900°C, and the blank test between 600 and 900°C, respectively. The detailed explanation for each value can be found in section 5.4.1. PUF samples were collected from blank runs between the 600° and 900°C test runs to measure the carryover between the tests on a single fluorocarbon product done at 600°C and 900°C.

Table 5.4.5.2. Flow Rate Profile for Combustion Test at 600°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)		Total Flow Rate (ml/min)	Volume (ml)
	Air	Air	CH_4		
0 – 60	9.69	0.85	0.21	10.75	10.75
60 – 82[a]	0.00	0.00	0.00	0.00	0.00
82 – 154	9.69	0.85	0.21	10.75	12.90
154 – 164	9.69	0.85 → 4.63[b]	0.21	10.75 → 14.53	2.11
164 – 174	9.69	4.63	0.21	14.53	2.42
174 - 194	8.31 (He)[c]	4.53 (He)[d]	0.00	12.84	4.28
				Total volume passed through reactor (ml)	32.46[e]
				Total volume passed through PUF (ml)	29.59[f]
				Total volume used for off-line GC/MS SO_2 quantitative analysis (ml)	21.71[g]

[a] System opened due to sample insertion. Assuming no outlet flow. [b] Linear increase (approximate). [c,d] Switched to helium for sweep. [e] Total carrier flow volume that passed through the reactor. [f] Total carrier flow volume that passed through PUFs. [g] Volume used to calculate total amount of SO_2 recovered using off-line GC/MS system.

Table 5.4.5.3. Flow Rate Profile for Combustion Test at 900°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)		Total Flow Rate (ml/min)	Volume (ml)
	Air	Air	CH_4		
0 – 60	7.06	0.66	0.16	7.88	7.88
60 – 83[a]	0.00	0.00	0.00	0.00	0.00
83 – 177	7.06	0.66	0.16	7.88	12.35
177 – 187	7.06	0.66 → 4.63[b]	0.16	7.88 → 11.85	1.64
187 – 197	7.06	4.63	0.16	11.85	1.98
197 - 217	6.05 (He)[c]	4.53 (He)[d]	0	10.58	3.53
				Total volume passed through reactor (ml)	27.37[e]
				Total volume passed through PUF (ml)	24.14[f]
				Total volume used for off-line GC/MS SO_2 quantitative analysis (ml)	19.49[g]

[a] System opened due to sample insertion. Assuming no outlet flow. [b] Linear increase (approximate). [c,d] Switched to helium for sweep. [e] Total carrier flow volume that passed through the reactor. [f] Total carrier flow volume that passed through PUFs. [g] Volume used to calculate total amount of SO_2 recovered using off-line GC/MS system.

Table 5.4.5.4. Flow Rate Profile for Blank Analysis between 600 and 900°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)		Total Flow Rate (ml/min)	Total Volume (ml)	Sampled Volume[d] (ml)
	Air	Air	CH_4			
0 – 120	9.69	0.85	0.00	10.54	21.08	19.08
120 – 130	9.69	0.85 → 4.63[a]	0.00	10.54 → 14.32	2.07	1.91
130 – 140	9.69	4.63	0.00	14.32	2.39	2.22
140 - 160	8.89 (He)[b]	4.53 (He)[c]	0.00	12.84	4.28	3.95
				Total Volume (ml)	29.82	27.15

[a] Linear increase (approximate). [b,c] Switched to helium for sweep. [d] Sampled volume for PUF and Tedlar bag collection.

5.4.5.1. In-line GC/MS Analysis: Figure 5.4.5.1 shows the total ion chromatogram for combustion at 600°C. The first peak at 0.5 to 1.9 min. was identified as pentafluoroethane and the second peak at 1.9 to 2.8 was identified as sulfur dioxide. The peak at 6.9 min. corresponded to carbon disulfide. The peaks at 10.4, 10.6, and 10.8 corresponded to benzene, difluorobenzene, and fluorobenzene, respectively. The wide peak appeared at 10.9 to 12.5 min and following background corresponded to tetrafluorosilane. Figure 5.4.5.2 shows the total ion chromatogram for combustion at 900°C. The first peak at 0.2 to 1.3 min. was identified as pentafluoroethane and the second peak at 1.9 to 2.4 min. was identified as sulfur dioxide. The largest peak at 12.2 to 12.8 min. and following high background was attributed to tetrafluorosilane. The peak at 14.0 min. was not clearly identified.

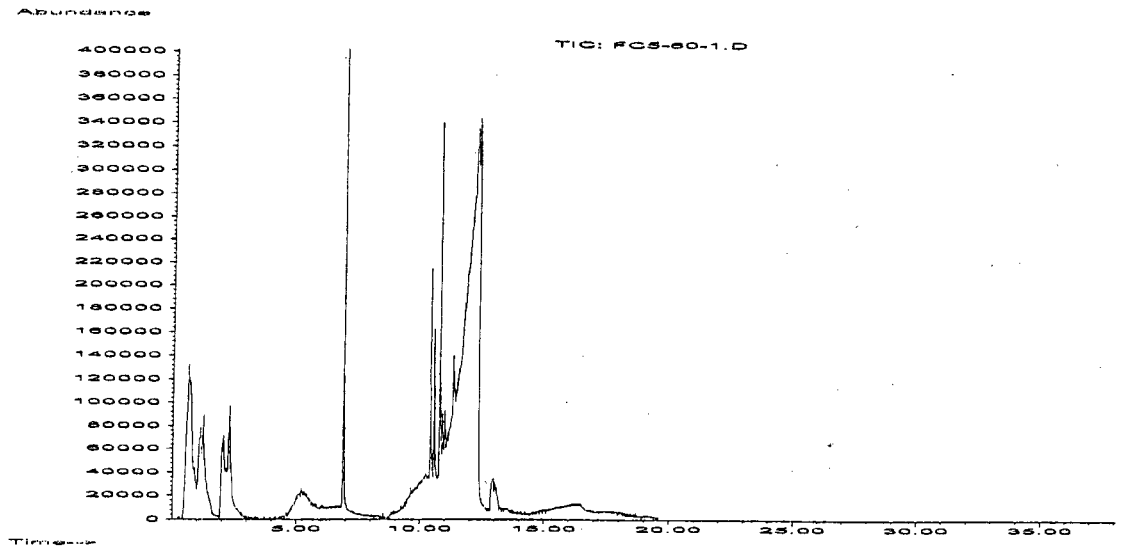

Figure 5.4.5.1. In-line GC/MS Ion Chromatogram for at 600°C

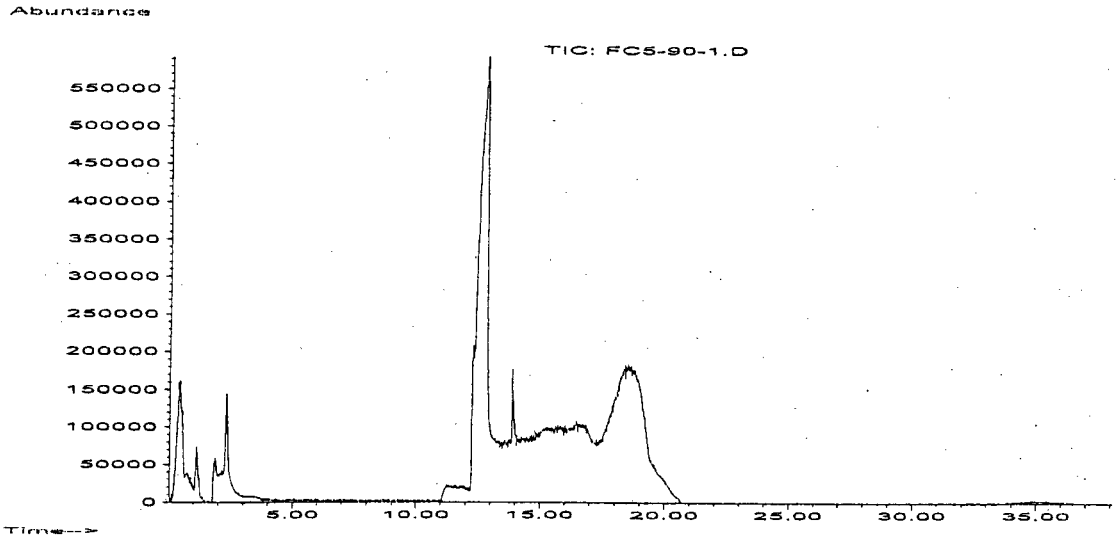

Figure 5.4.5.2. In-line GC/MS Ion Chromatogram for at 900°C

5.4.5.2. Off-line GC/MS Analysis: Figure 5.4.5.3 shows the total ion chromatogram for off-line GC/MS analyses for combustion at 600°C. The largest peak at the beginning is associated with air. The small peak next to air at 0.97 min. corresponds to 1,1-difluoroethene. The next small peak at 1.65 min. corresponds to pentafluoroethane. The second largest peak at 3.0 min. corresponds to sulfur dioxide. The small peak at 4.8 min. corresponds to difluorodimethylsilane. Figure 5.4.5.4 shows the total ion chromatogram for off-line GC/MS analyses for combustion at 900°C. Similar results were obtained. The largest peak at the beginning is associated with air. The second peak at 3.0 min. corresponds to sulfur dioxide. The small peak at 4.8 min. corresponds to difluorodimethylsilane.

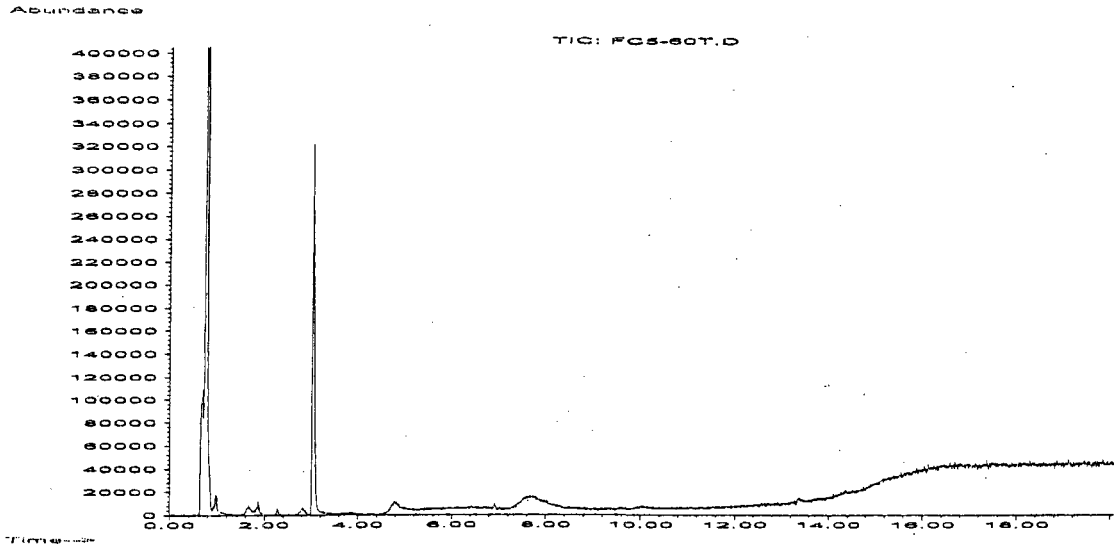

Figure 5.4.5.3. Off-line GC/MS Ion Chromatogram for at 600°C

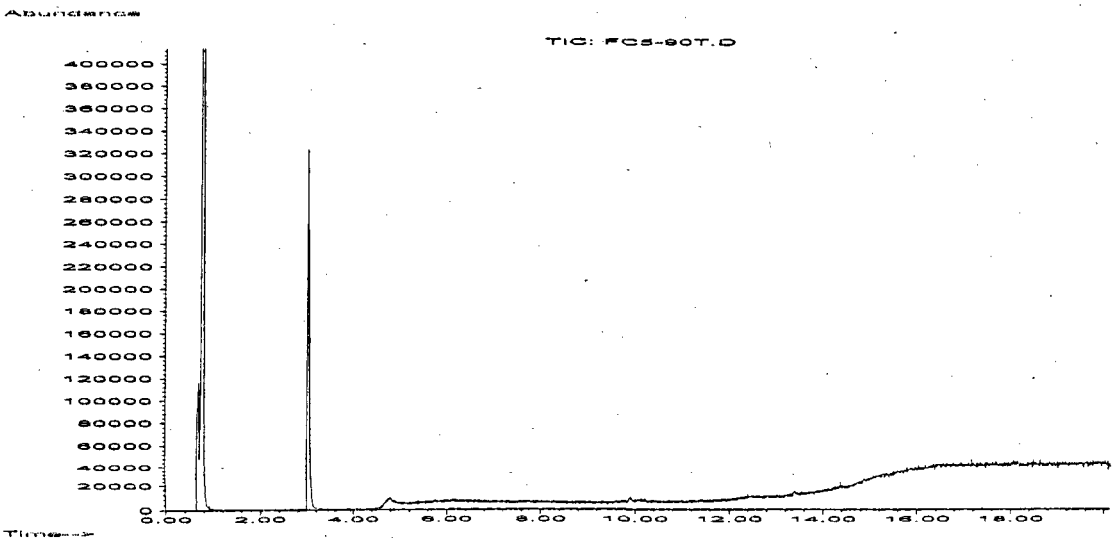

Figure 5.4.5.4. Off-line GC/MS Ion Chromatogram for at 900°C

5.4.5.3 LC-MS Analysis of Extracts: Table 5.4.5.5 shows the analytical results of the reactor/transfer line extraction samples. No detectable amount of PFOS, PFBS, was found.

Table 5.4.5.5. Methanol Extraction Results for Combustion Test

Extraction	PFOS(pg/μl)	PFOS(μg)	PFBS(pg/μl)	PFBS(μg)		
1st	<5.00	<0.035	<5.05	<0.032	<4.96	<0.028
2nd	<5.00	<0.035	<5.05	<0.032	<4.96	<0.028

5.4.5.4. LC-MS Analysis of PUF Cartridges: Table 5.4.5.6 shows the analytical results for the PUF sampling cartridges. No detectable amount of PFOS, PFBS, was found.

Table 5.4.5.6. PUF Extraction Results for Combustion Test

Temp (°C)	Media	PFOS (pg/μl)	PFOS (μg)	PFBS (pg/μl)	PFBS (μg)	(pg/μg)	(μl)
600	PUF (1st)	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10
	PUF (2nd)	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10
900	PUF (1st)	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10
	PUF (2nd)	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10

5.4.6. PFBS Combustion Test

Table 5.4.6.1 shows net amount of sample gasified for PFBS combustion tests. The sample probe was weighed before and after the combustion tests.

Table 5.4.6.1. Net Amount of Gasified Sample for PFBS Combustion Test

Temperature (°C)	Usage	Loaded Mass (mg)	Remaining (mg)	Net Amount of Gasified Sample (mg)
600	PUF[a]	0.64	0.30	0.34
	TB[b]	0.59	0.11	0.48
900	PUF	0.62	0.16	0.46
	TB	0.59	0.17	0.42

[a] In-line GC/MS analysis and off-gas collection using PUF. [b] Off-line GC/MS analysis using Tedlar Bag.

Table 5.4.6.2, 5.4.6.3, and 5.4.6.4 show flow rate profiles used for PFBS combustion tests at 600 and 900°C, and the blank test between 600 and 900°C, respectively. The detailed explanation for each value can be found in section 5.4.1. PUF samples were collected from blank runs between the 600 and 900°C test runs to measure the carryover between the tests on a single fluorocarbon product done at 600 and 900°C.

Table 5.4.6.2. Flow Rate Profile for PFBS Combustion Test at 600°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)		Total Flow Rate (ml/min)	Volume (ml)
	Air	Air	CH_4		
0 – 60	9.79	0.83	0.22	10.84	10.84
60 – 80[a]	0.00	0.00	0.00	0.00	0.00
80 – 152	9.79	0.83	0.22	10.84	13.01
152 – 162	9.79	0.83 → 4.63[b]	0.22	10.84 → 14.64	2.12
162 – 172	9.79	4.63	0.22	14.64	2.44
172 - 192	8.31 (He)[c]	4.53 (He)[d]	0.00	12.97	4.32
				Total volume passed through reactor (ml)	32.73[e]
				Total volume passed through PUF (ml)	29.87[f]
				Total volume used for off-line GC/MS SO_2 quantitative analysis (ml)	21.89[g]

[a] System opened due to sample insertion. Assuming no outlet flow. [b] Linear increase (approximate). [c,d] Switched to helium for sweep. [e] Total carrier flow volume that passed through the reactor. [f] Total carrier flow volume that passed through PUFs. [g] Volume used to calculate total amount of SO_2 recovered using off-line GC/MS system.

Table 5.4.6.3. Flow Rate Profile for PFBS Combustion Test at 900°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)		Total Flow Rate (ml/min)	Volume (ml)
	Air	Air	CH_4		
0 – 60	7.14	0.65	0.17	7.96	7.96
60 – 80[a]	0.00	0.00	0.00	0.00	0.00
80 – 174	7.14	0.65	0.17	7.96	12.47
174 – 184	7.14	0.65 → 4.63[b]	0.17	7.96 → 11.94	1.66
184 – 194	7.14	4.63	0.17	11.94	1.99
194 - 214	6.24 (He)[c]	4.53 (He)[d]	0.00	10.77	3.59
				Total volume passed through reactor (ml)	27.67[e]
				Total volume passed through PUF (ml)	24.44[f]
				Total volume used for off-line GC/MS SO_2 quantitative analysis (ml)	19.71[g]

[a] System opened due to sample insertion. Assuming no outlet flow. [b] Linear increase (approximate). [c,d] Switched to helium for sweep. [e] Total carrier flow volume that passed through the reactor. [f] Total carrier flow volume that passed through PUFs. [g] Volume used to calculate total amount of SO_2 recovered using off-line GC/MS system.

Table 5.4.6.4. Flow Rate Profile for Blank Analysis between 600 and 900°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)		Total Flow Rate (ml/min)	Total Volume (ml)	Sampled Volume[d] (ml)
	Air	Air	CH_4			
0 – 120	9.79	0.83	0.00	10.62	21.24	19.24
120 – 130	9.79	0.83 → 4.63[a]	0.00	10.62 → 14.42	2.09	1.92
130 – 140	9.79	4.63	0.00	14.42	2.40	2.24
140 - 160	8.44 (He)[b]	4.53 (He)[c]	0.00	12.97	4.32	3.99
				Total Volume (ml)	30.05	27.39

[a] Linear increase (approximate). [b,c] Switched to helium for sweep. [d] Sampled volume for PUF and Tedlar bag collection.

5.4.6.1. In-line GC/MS Analysis: Figure 5.4.6.1 shows the total ion chromatogram for PFBS combustion at 600°C. The peak at 0.6 was identified as pentafluoroethane and that at 1.0 min., which has strong 85 m/z signal, was not identified. Tetrafluorosilane is not likely because of the different retention time. The peak at 1.7 to 2.5 min. corresponds to sulfur dioxide. The largest peak at 10.0 to 12.0 min. corresponds to tetrafluorosilane. Figure 5.4.6.2 shows the total ion chromatogram for PFBS combustion at 900°C. The first peak at 1.8 to 2.5 min. corresponds to sulfur dioxide. The peak at 10.6 corresponds to benzene. The largest peak at 14.2 min. and following background correspond to tetrafluorosilane.

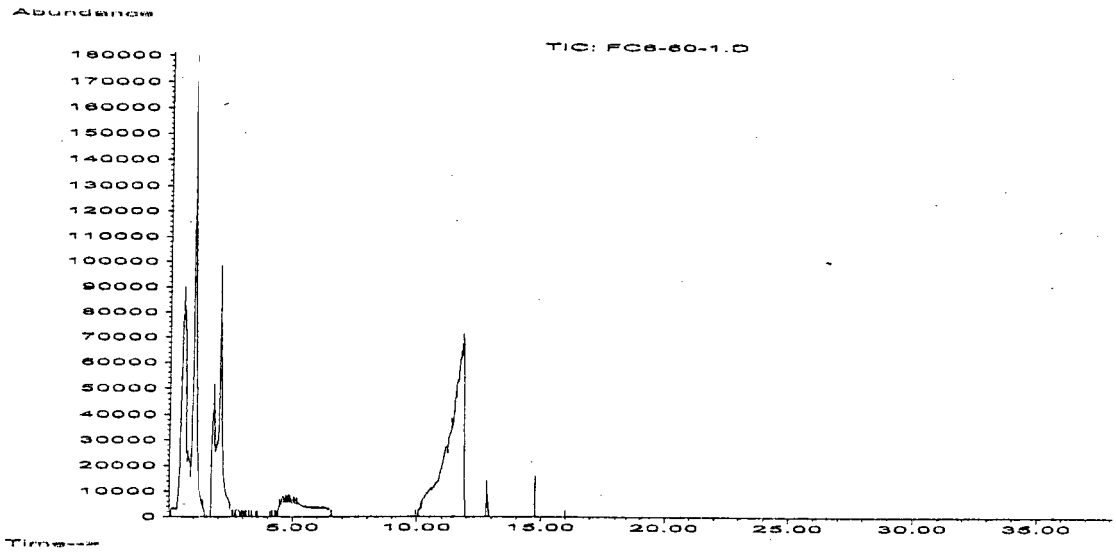

Figure 5.4.6.1. In-line GC/MS Ion Chromatogram for PFBS at 600°C

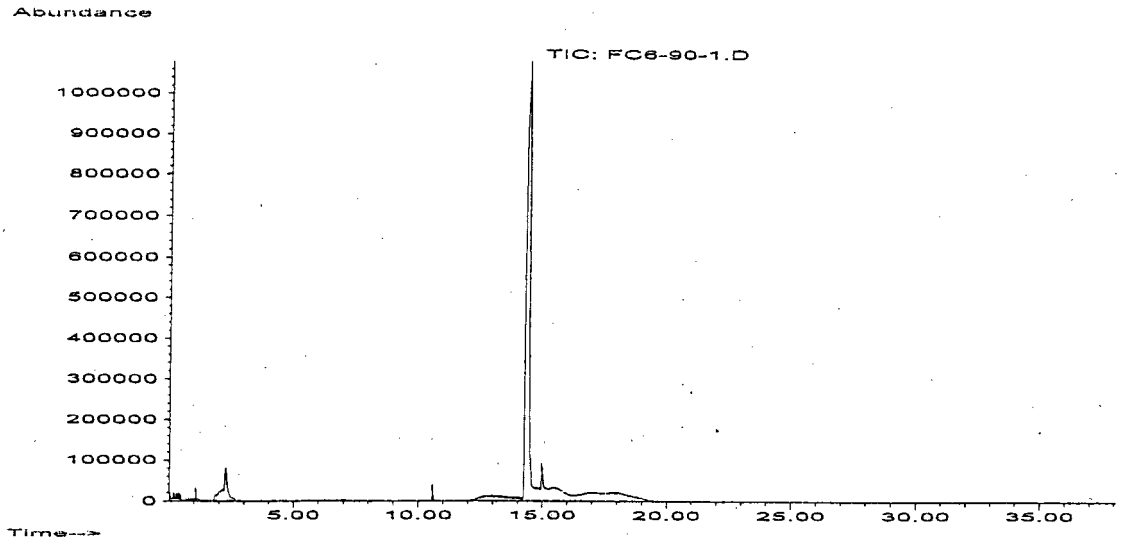

Figure 5.4.6.2. In-line GC/MS Ion Chromatogram for PFBS at 900°C

5.4.6.2. Off-line GC/MS Analysis: Figure 5.4.6.3 shows the total ion chromatogram for off-line GC/MS analyses for PFBS combustion at 600°C. The largest peak at the beginning is associated with air. The second peak at 3.0 min. corresponds to sulfur dioxide. Figure 5.4.6.4 shows the total ion chromatogram for off-line GC/MS analyses for PFBS combustion at 900°C. Similar results were obtained. The largest peak at the beginning is associated with air. The second peak at 3.0 min. corresponds to sulfur dioxide.

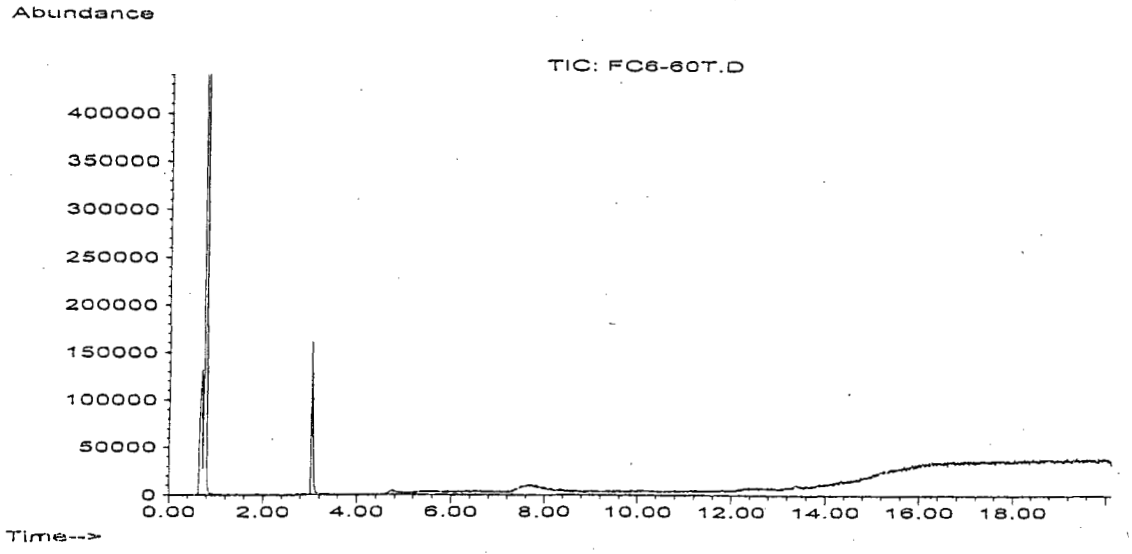

Figure 5.4.6.3. Off-line GC/MS Ion Chromatogram for PFBS at 600°C

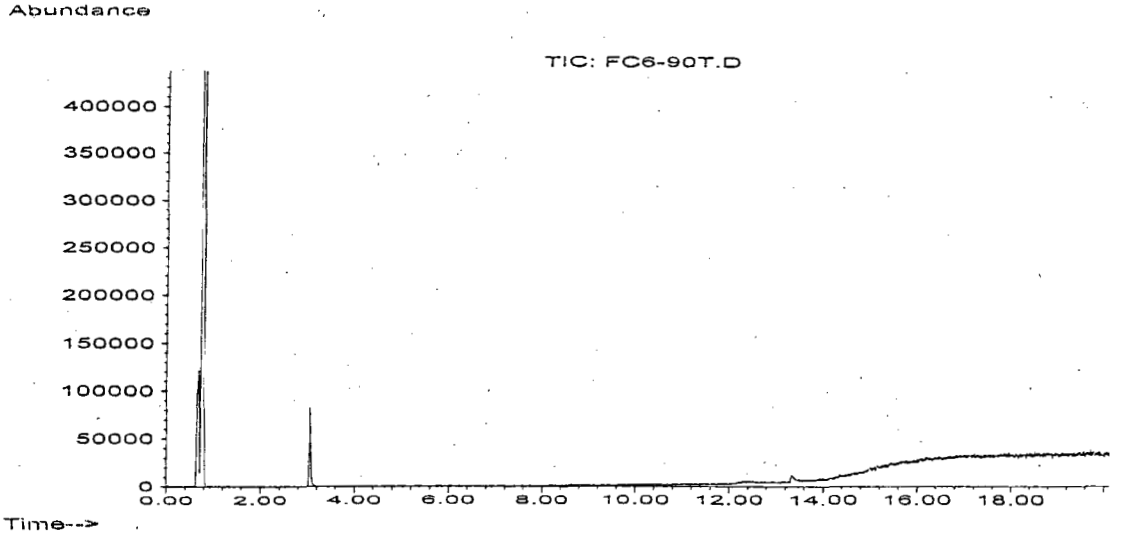

Figure 5.4.6.4. Off-line GC/MS Ion Chromatogram for PFBS at 900°C

5.4.6.3. LC-MS Analysis of Extracts: Table 5.4.6.5 shows the analytical results of the reactor/transfer line extraction samples. The first and second extracts of the PFBS reactor/transfer line done after the 900°C run totaled to about 0.22% of the PFBS added. A small amount of was also found from the extracts. The contamination source may be the outer pyroprobe surface (not the insert, which is replaced with each test) where combustion was conducted in the previous test. New reactor/transfer lines were used for each combustion test. The reactor/transfer line extraction for combustion test was performed prior to PFBS combustion extraction, but no was detected from the prior extraction. The extraction system tubing was cleaned following every sample extraction.

Table 5.4.6.5. Methanol Extraction Results for PFBS Combustion Test

Extraction	PFOS(pg/μl)	PFOS(μg)	PFBS(pg/μl)	PFBS(μg)		
1st	<5.00	<0.035	169	1.1	15.4	0.087
2nd	<5.00	<0.035	60.3	0.39	<4.96	<0.028

5.4.6.4. LC-MS Analysis of PUF Cartridges: Table 5.4.6.6 shows the analytical results for the PUF sampling cartridges. A little less than 0.6%[1] of PFBS was detected at 600°C and surprisingly, a larger 1.1% amount of PFBS was detected from the 900°C test. The distribution between the 1st and 2nd PUF was about equal at 600°C, but 97% of PFBS was captured in the first PUF at 900°C. An amount of carryover equivalent to 0.066% of PFBS added in the preceding 600°C tests was extracted from the PUF in the PFBS interim blank. In addition, an amount of equivalent to 0.09% of the that would have been added in a test was found in the PFBS interim blank. The presence of the is another indication of possible low level cross contamination between tests.

Table 5.4.6.6. PUF Extraction Results for PFBS Combustion Test

Temp (°C)	Extraction	PFOS (pg/μl)	PFOS (μg)	PFBS (pg/μl)	PFBS (μg)	(pg/μl)	(μg)
600	PUF (1st)	<5.00	<0.12	84.5	2.0	<4.96	<0.10
	PUF (2nd)	<5.00	<0.12	85.6	2.0	<4.96	<0.10
900	PUF (1st)	<5.00	<0.12	320	7.4	<4.96	<0.10
	PUF (2nd)	<5.00	<0.12	9.63	0.22	<4.96	<0.10
Interim blank	PUF (1st)	<5.00	<0.12	19.3	0.45	26.2	0.54

5.4.7. PFOS Combustion Test

Table 5.4.7.1 shows net amount of sample gasified for PFOS combustion tests. The sample probe was weighed before and after the combustion tests.

Table 5.4.7.1. Net Amount of Gasified Sample for PFOS Combustion Test

Temperature (°C)	Usage	Loaded Mass (mg)	Remaining (mg)	Net Amount of Gasified Sample (mg)
600	PUF[a]	0.47	0.02	0.45
	TB[b]	0.48	0.10	0.38
900	PUF	0.50	0.00	0.50
	TB	0.50	0.00	0.50

[a] In-line GC/MS analysis and off-gas collection using PUF. [b] Off-line GC/MS analysis using Tedlar Bag.

[1] The percentages that indicate the sample recovery here and hereafter are not corrected for the fraction of air flow that was diverted to the in-line GC/MS. The correction for this fraction is too complicated and ambiguous to make accurately because of the complexity of the flow scheme, mainly due to changes in both concentration and split ratio with time. If corrected, these recoveries would likely be 10 to 15 percent higher.

Tables 5.4.7.2, 5.4.7.3 and 5.4.7.4 show flow rate profiles used for PFOS combustion tests at 600 and 900°C, and the blank test between 600 and 900°C, respectively. The detailed explanation for each value can be found in section 5.4.1. PUF cartridge samples were collected from blank runs between the 600 and 900°C test runs to measure the carryover between the tests on a single fluorocarbon product done at 600 and 900°C.

Table 5.4.7.2. Flow Rate Profile for PFOS Combustion Test at 600°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)		Total Flow Rate (ml/min)	Volume (ml)
	Air	Air	CH_4		
0 – 60	9.86	0.85	0.21	10.92	10.92
60 – 85[a]	0.00	0.00	0.00	0.00	0.00
85 – 157	9.86	0.85	0.21	10.92	13.10
157 – 167	9.86	0.85 → 4.63[b]	0.21	10.92 → 14.70	2.14
167 – 177	9.86	4.63	0.21	14.70	2.45
177 - 197	8.61 (He)[c]	4.53 (He)[d]	0.00	13.14	4.38
			Total volume passed through reactor (ml)		32.99[e]
			Total volume passed through PUF (ml)		30.12[f]
		Total volume used for off-line GC/MS SO_2 quantitative analysis (ml)			22.07[g]

[a] System opened due to sample insertion. Assuming no outlet flow. [b] Linear increase (approximate). [c,d] Switched to helium for sweep. [e] Total carrier flow volume that passed through the reactor. [f] Total carrier flow volume that passed through PUFs. [g] Volume used to calculate total amount of SO_2 recovered using off-line GC/MS system.

Table 5.4.7.3. Flow Rate Profile for PFOS Combustion Test at 900°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)		Total Flow Rate (ml/min)	Volume (ml)
	Air	Air	CH_4		
0 – 60	7.12	0.65	0.16	7.93	7.93
60 – 85[a]	0.00	0.00	0.00	0.00	0.00
85 – 179	7.12	0.65	0.16	7.93	12.42
179 – 189	7.12	0.65 → 4.63[b]	0.16	7.93 → 11.91	1.65
189 – 199	7.12	4.63	0.16	11.91	1.99
199 - 219	6.15 (He)[c]	4.53 (He)[d]	0	10.68	3.56
			Total volume passed through reactor (ml)		27.55[e]
			Total volume passed through PUF (ml)		24.32[f]
		Total volume used for off-line GC/MS SO_2 quantitative analysis (ml)			19.62[g]

[a] System opened due to sample insertion. Assuming no outlet flow. [b] Linear increase (approximate). [c,d] Switched to helium for sweep. [e] Total carrier flow volume that passed through the reactor. [f] Total carrier flow volume that passed through PUFs. [g] Volume used to calculate total amount of SO_2 recovered using off-line GC/MS system.

Table 5.4.7.4. Flow Rate Profile for Blank Analysis between 600 and 900°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)		Total Flow Rate (ml/min)	Total Volume (ml)	Sampled Volume[d] (ml)
	Air	Air	CH_4			
0 – 120	9.86	0.85	0.00	10.71	21.42	19.42
120 – 130	9.86	0.85 → 4.63[a]	0.00	10.71 → 14.49	2.10	1.93
130 – 140	9.86	4.63	0.00	14.49	2.42	2.25
140 - 160	8.61 (He)[b]	4.53 (He)[c]	0.00	13.14	4.38	4.05
				Total Volume (ml)	30.32	27.65

[a] Linear increase (approximate). [b,c] Switched to helium for sweep. [d] Sampled volume for PUF and Tedlar bag collection.

5.4.7.1. In-line GC/MS Analysis: Figure 5.4.7.1 and 5.4.7.2 show total ion chromatograms for PFOS combustion at 600 and 900°C, respectively. A single sulfur dioxide peak was the only identifiable peak for both combustion tests. No tetrafluorosilane peak was observed for PFOS combustion tests. It is not clear why the total ion chromatograms for PFOS combustion at 600 and 900°C differ from the others. The MSD source might have suffered from a loss of sensitivity due to the repetitive, heavy-duty use. No attempts were made to clean the MSD source because the cleaning process requires MS signal tuning and the recalibration of all standard gases previously conducted, which was not feasible at this late stage of the testing.

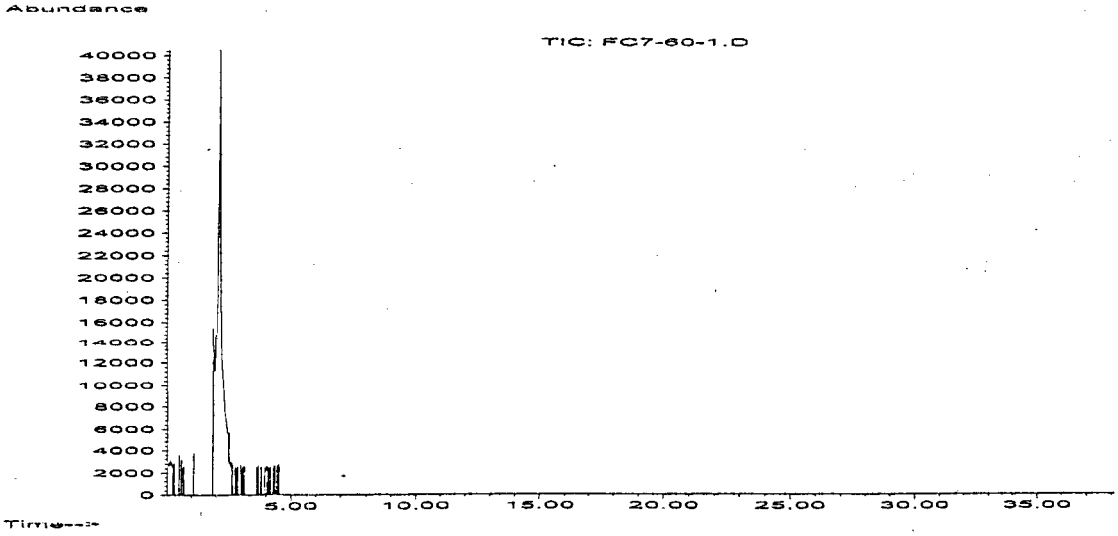

Figure 5.4.7.1. In-line GC/MS Ion Chromatogram for PFOS at 600°C

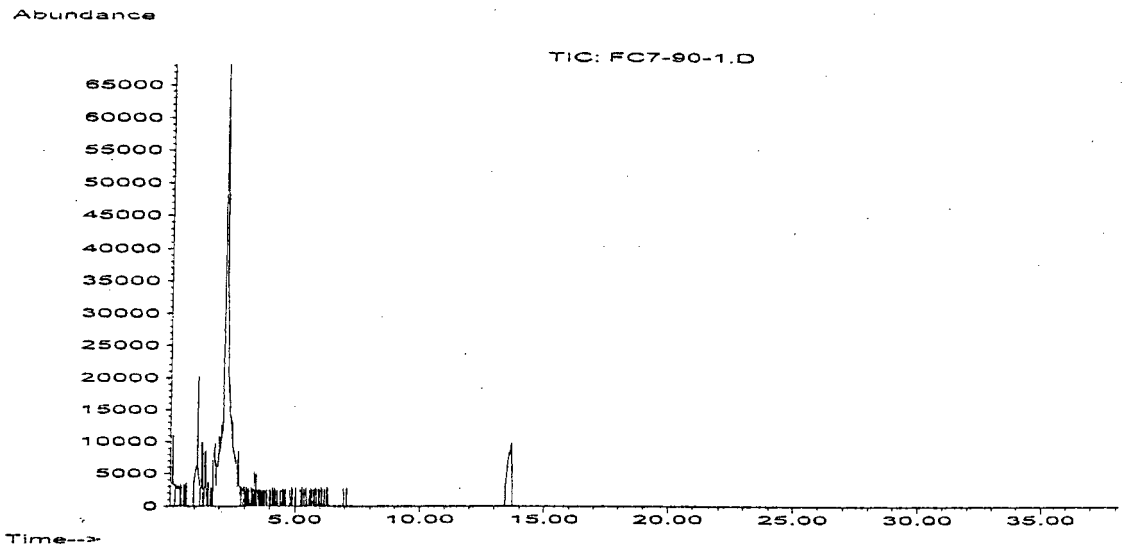

Figure 5.4.7.2. In-line GC/MS Ion Chromatogram for PFOS at 900°C

5.4.7.2. Off-line GC/MS Analysis: Figure 5.4.7.3 shows the total ion chromatogram for off-line GC/MS analyses for PFOS combustion at 600°C. The largest peak at the beginning is associated with air. The second peak at 1.0 min. was identified as 1,1-difluoroethene. The peak at 3.0 min. was identified as sulfur dioxide. Figure 5.4.7.4 shows the total ion chromatogram for off-line GC/MS analyses for PFOS combustion at 900°C. Similar results were obtained. The largest peak at the beginning is associated with air. The second peak at 3.0 min. corresponds to sulfur dioxide.

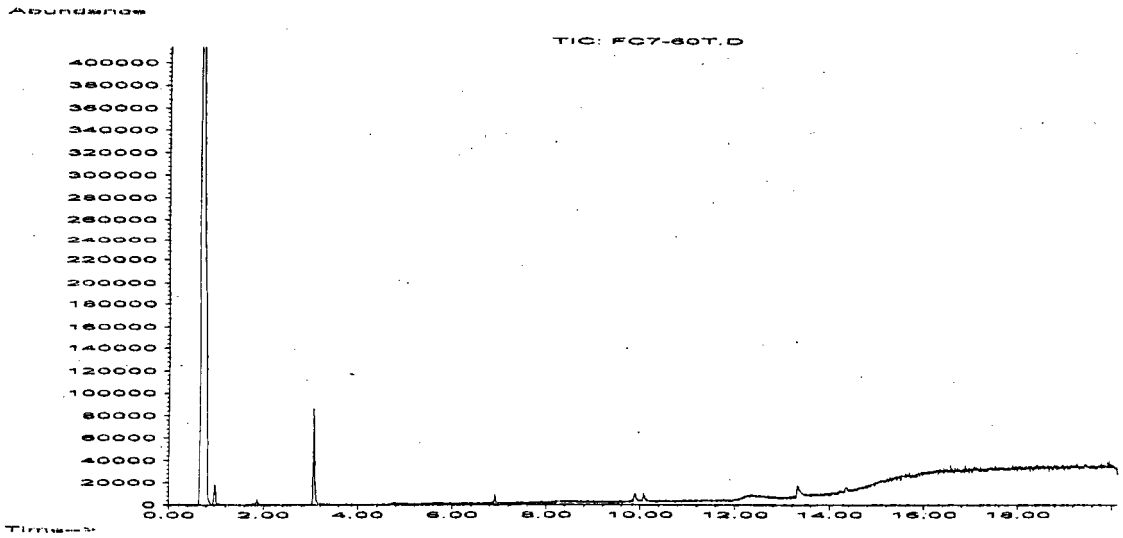

Figure 5.4.7.3. Off-line GC/MS Ion Chromatogram for PFOS at 600°C

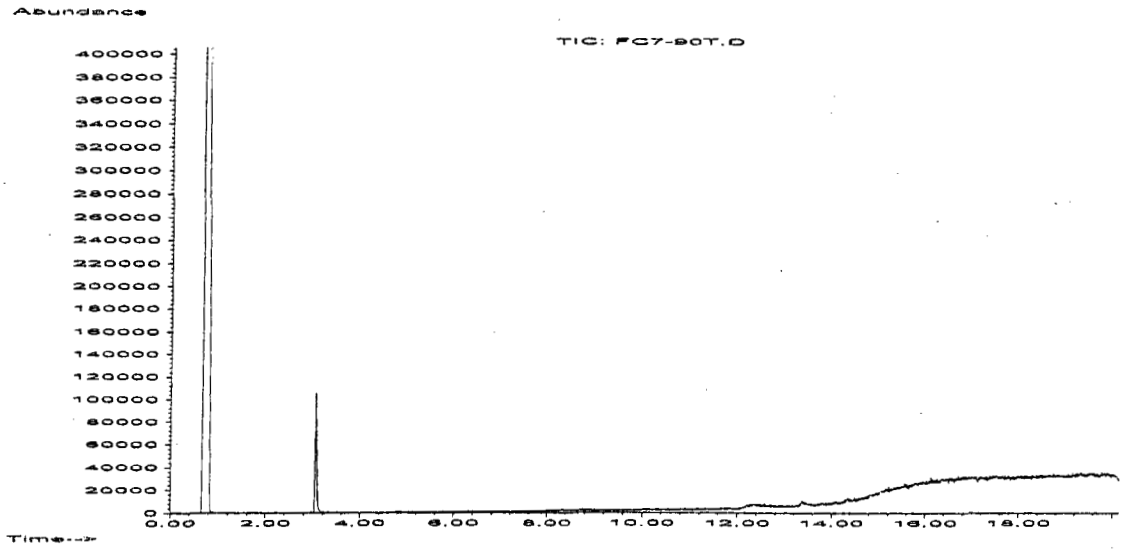

Figure 5.4.7.4. Off-line GC/MS Ion Chromatogram for PFOS at 900°C

5.4.7.3. LC-MS Analysis of Extracts: Table 5.4.7.5 shows the analytical results of the reactor/ transfer line extraction samples. Extracts of reactor/transfer line tubing after the 900°C test summed to only about 0.04% of the PFOS added. A small amount of PFBS, 0.04 μg, was detected from the extract, which could be formed during PFOS combustion or could have been carryover from the previous PFBS combustion tests.

Table 5.4.7.5. Methanol Extraction Results for PFOS Combustion Test

Extraction	PFOS(pg/μl)	PFOS(μg)	PFBS(pg/μl)	PFBS(μg)		
1st	15.4	0.11	7.11	0.045	<4.96	<0.028
2nd	8.61	0.059	<5.05	<0.032	<4.96	<0.028

5.4.7.4. LC-MS Analysis of PUF Cartridges: Table 5.4.7.6 shows the analytical results for the PUF sampling cartridges. The amount of PFOS captured in the PUF was less than 0.4 % of the PFOS added at 600°C. Only about 0.05% was captured by the PUFs at 900°C. Surprisingly, somewhat larger amounts of PFOS were extracted from the second PUF in a two-PUF series at both 600°C and 900°C. This suggests that some PFOS could have passed completely through the system, but in the third transfer efficiency tests, much larger amounts of PFOS and PFBS were captured in the first PUF in the series showing that the first PUF typically collects more. An amount of carryover equivalent to 0.026% of PFOS added in the preceding 600°C tests was extracted from the PUF in the PFOS interim blank. A small amount of PFBS was found from the combustion test at 900°C, which could have been carryover or a combustion byproduct of PFOS combustion.

Table 5.4.7.6. PUF Extraction Results for PFOS Combustion Test

Temp (°C)	Extraction	PFOS (pg/μl)	PFOS (μg)	PFBS (pg/μl)	PFBS (μg)	L-16271 (pg/μl)	L-16271 (μg)
600	PUF (1^{st})	25.1	0.62	<5.05	<0.12	<4.96	<0.10
	PUF (2^{nd})	64.0	1.6	<5.05	<0.12	<4.96	<0.10
900	PUF (1^{st})	4.31	0.11	<5.05	<0.12	<4.96	<0.10
	PUF (2^{nd})	9.01	0.22	25.8	0.60	<4.96	<0.10

5.5. Revised Chemical Composition of

Table 5.5.2 shows the changes in the necessary amount of sample that have the equivalent amount of fluorine in 0.5 mg of PFOS and the corresponding stoichiometric amount of air. The actual amount of samples gasified for combustion tests were 1.88 to 2.10 mg and 2.76 to 2.94 mg, respectively, which were ca. 10% different from the ideal amounts. This difference is well within the overall error of the measurements and does not impact the validity of the test results.

Table 5.5.2. Correction of Amount of Sample That Contains Equivalent Amount of Fluorine in 0.5 mg of PFOS

5.6. 2^{nd} Heated Blank Combustion Analysis

After the combustion tests for the seven compounds were completed, the heated blank reactor/ transfer line tubing was analyzed again to examine system cross contamination at temperatures of 600 and 900°C. In-line GC/MS analysis, off-line GC/MS analysis using Tedlar bags, and

PUF cartridge sampling were conducted. The same process used for the first heated blank analysis before the sample combustion tests was performed for this second heated blank analysis. The PUF samples were sent to 3M Environmental Laboratory for LC/MS analysis.

5.6.1. In-line GC/MS Analysis

Table 5.6.1 and 5.6.2 shows flow rate profile and carrier flow volume used for heated blank analysis at 600 and 900°C, respectively. Figure 5.6.1 and 5.6.2 shows total ion chromatograms for reactor temperatures at 600 and 900°C, respectively. The chromatograms show only background noise and no contamination was found for either temperature.

Table 5.6.1. Flow Rate Profile for Heated Blank Analysis at 600°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)	Total Flow Rate (ml/min)	Total Volume (ml)	Sampled Volume[d] (ml)
0 – 120	10.0	0.81	10.81	21.62	19.62
120 – 130	10.0	0.81 → 4.63[a]	10.81 → 14.63	2.12	1.95
130 – 140	10.0	4.63	14.63	2.44	2.27
140 – 160	8.83 (He)[b]	4.53 (He)[c]	13.36	4.45	4.12
			Total Volume (ml)	30.63	27.97

[a] Linear increase (approximate). [b,c] Switched to helium for sweep. [d] Sampled volume for PUF and Tedlar bag collection.

Table 5.6.2. Flow Rate Profile for Heated Blank Analysis at 900°C

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (mi/min)	Total Flow Rate (ml/min)	Total Volume (ml)	Sampled Volume[d] (ml)
0 – 150	7.11	0.62	7.73	19.33	16.83
150 – 160	7.11	0.62 → 4.63[a]	7.73 → 11.74	1.62	1.46
160 – 170	7.11	4.63	11.74	1.96	1.79
170 – 190	6.16 (He)[b]	4.53 (He)[c]	10.69	3.56	3.23
			Total Volume (ml)	26.47	23.30

[a] Linear increase (approximate). [b,c] Switched to helium for sweep. [d] Sampled volume for PUF and Tedlar bag collection.

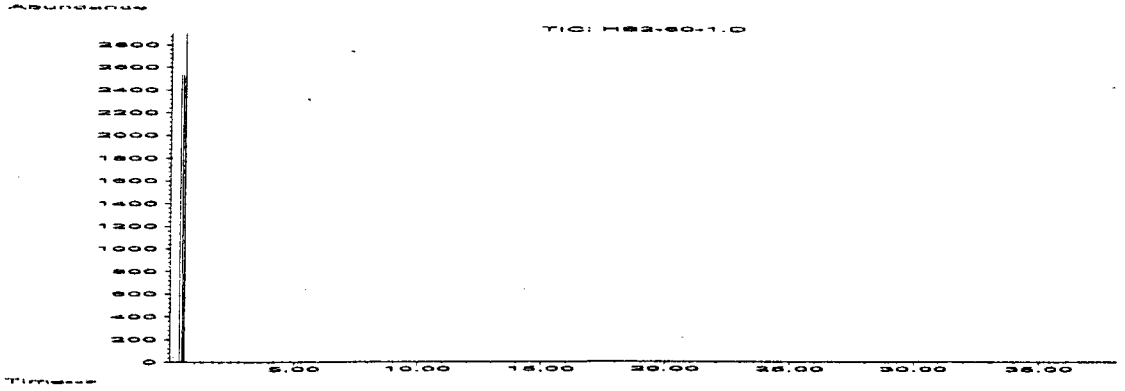

Figure 5.6.1. In-line GC/MS Ion Chromatogram for Heated Blank at 600°C

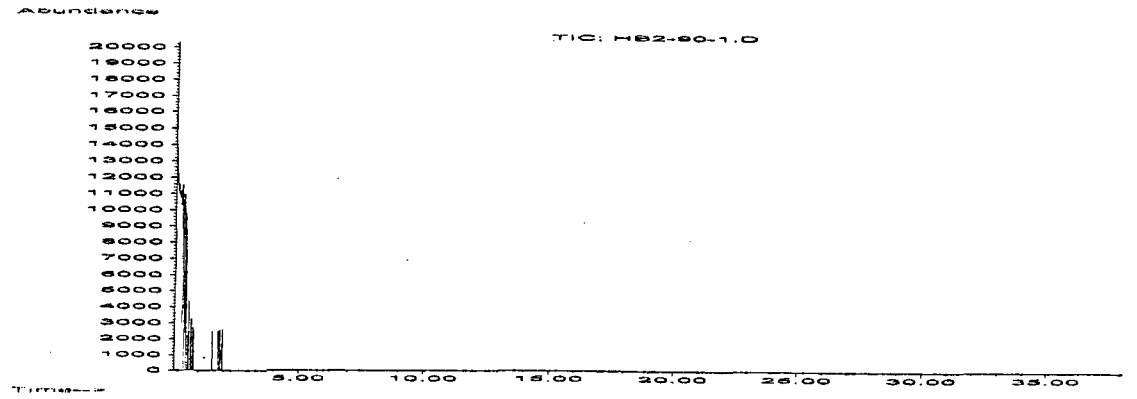

Figure 5.6.2. In-line GC/MS Ion Chromatogram for Heated Blank at 900°C

5.6.2. Off-line GC/MS Analysis

Figure 5.6.3 and 5.6.4 show total ion chromatograms for the heated blank at 600 and 900°C respectively. The large peaks at the beginning are associated with air. No other peaks were observed.

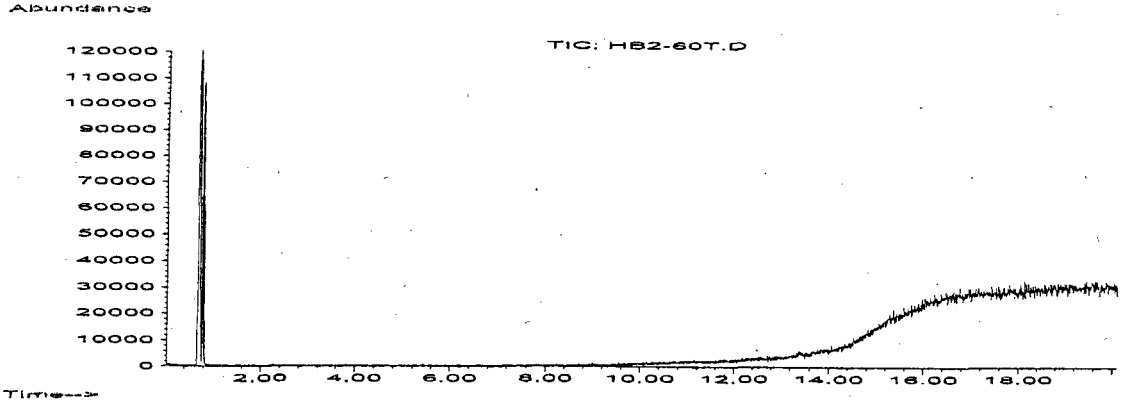

Figure 5.6.3. Off-line GC/MS Ion Chromatogram for Heated Blank at 600°C

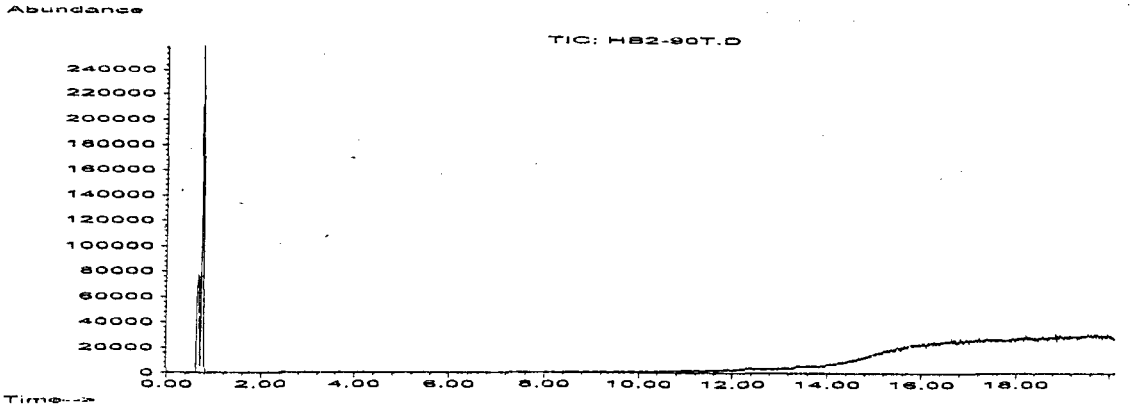

Figure 5.6.4. Off-line GC/MS Ion Chromatogram for Heated Blank at 900°C

5.6.3. LC-MS Analysis of PUF Cartridges

Table 5.6.3 shows the analytical results for the PUF sampling cartridges. No cross contamination was detected.

Table 5.6.3. PUF Extraction Results for Heated Blank Analysis

Temp (°C)	PFOS(pg/μl)	PFOS(μg)	PFBS(pg/μl)	PFBS(μg)		
600	<10.0	<0.25	<10.1	<0.23	<4.96	<0.10
900	<10.0	<0.25	<10.1	<0.23	<4.96	<0.10

5.7. Transport Efficiency Tests for PFBS and PFOS

Sample transfer efficiency tests were conducted to investigate how efficiently PFOS, PFBS, and would be transferred through reactor/transfer line system. Three types of tests were conducted for each sample, which were described in the Phase III protocol and its addendum.

5.7.1. 1st Transport Efficiency Test

In the first transfer efficiency test, PFOS, PFBS, were volatilization in the pyroprobe chamber and the reactor and transfer lines were heated to 260°C. PUF cartridge sampling of the off-gases was performed. This test examines the transfer efficiency of samples gasified in the pyroprobe and transported through reactor. Table 5.7.1.1 shows the net amount of gasified sample for the 1st transfer efficiency test. Table 5.7.1.2 shows flow profiles used for , PFBS, and PFOS.

Table 5.7.1.1. Net Amount of Gasified Sample for 1st Transfer Efficiency Test

Sample	Loaded Mass (mg)	Remained after Gasification (mg)	Net Amount of Gasified Sample (mg)
	0.53	0.00	0.53
PFBS	0.54	0.00	0.54
PFOS	0.53	0.05	0.48

Table 5.7.1.2. Flow Rate Profile for 1st Transfer Efficiency Test[a]

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)	Total Flow Rate (ml/min)	Total Volume (ml)	Sampled Volume[c] (ml)
0 – 60	16.0	0.82	16.82	16.82	15.82
60 – 84	0.00	0.00	0.00	0.00	
84 – 156	16.0	0.82	16.82	20.18	18.98
156 – 166	16.0	0.82 → 4.53[b]	16.82 → 20.53	3.11	2.95
166 – 186	16.0	4.53	20.53	6.84	6.51
			Total Volume (ml)	46.95	44.26

[a] Helium was used for all carrier flow. [b] Linear increase (approximate). [c] Sampled volume for PUF collection.

Table 5.7.1.3 shows the PUF cartridge sampling results for , PFBS, and PFOS, respectively. No sample was recovered from the PUF cartridge. This result indicates that the

sample was either thermally dissociated in the pyroprobe chamber or the gasified sample was completely condensed in the pyroprobe/reactor transfer line tubing.

Table 5.7.1.3. PUF Extraction Results for 1st Transfer Efficiency Test

Sample	PUF Extracts	PFOS (pg/μl)	PFOS (μg)	PFBS (pg/μl)	PFBS (μg)	(pg/μg)	(μl)
	1st	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10
	2nd	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10
PFBS	1st	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10
	2nd	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10
PFOS	1st	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10
	2nd	<5.00	<0.12	<5.05	<0.12	<4.96	<0.10

5.7.2. 2nd Transfer Efficiency Test

To investigate the possibility that the sample condensed on the walls of the pyroprobe/reactor transfer line, the sample was collected directly from the pyroprobe upstream of the reactor. PUF sample cartridges were connected to the pyroprobe using the shortest possible transfer line. The pyroprobe and transfer line were extracted using methanol. Table 5.7.2.1 shows the net amount of gasified sample for 2nd transfer efficiency test. Table 5.7.2.2 shows flow profiles for PFBS, and PFOS 2nd transfer efficiency test, respectively.

Table 5.7.2.1. Net Amount of Gasified Sample for 2nd Transfer Efficiency Test

Sample	Loaded Mass (mg)	Remained after Gasification (mg)	Net Amount of Gasified Sample (mg)
	0.52	0.02	0.50
PFBS	0.60	0.16	0.44
PFOS	0.47	0.00	0.47

Table 5.7.2.2. Flow Rate Profile for 2nd Transfer Efficiency Test[a]

Time Period (sec)	Pyroprobe Flow Rate (ml/min)	Volume (ml)
0 – 60	0.63	0.63
60 – 82	0.00	0.00
82 – 176	0.63	0.99
176 – 186	0.63 → 4.53[b]	0.43
186 – 216	4.53	2.27
	Total Volume (ml)	4.32

[a] Helium was used for carrier flow. [b] Linear increase (approximate).

Table 5.7.2.3 shows the analytical results for the extracts. Table 5.7.2.4 shows the analytical results for PUF cartridge samples. Substantial amounts, 3.4% of PFOS and 2.6 % of PFBS, were found in the pyroprobe transfer line extracts. Very little was detected in the PUF cartridge samples. This test shows that measurable amounts of PFOS and PFBS survive pyrolysis conditions of the pyroprobe, and enter the heated transfer lines up to the reactor. Larger amounts

of PFOS and PFBS condense in the heated transfer lines downstream of the pyroprobe and upstream of the high-temperature reactor.

Analytical results on the 2nd transfer efficiency test also showed some indications of cross contamination. Significant amounts of PFOS were found in the first PUF (equivalent to 0.5%) and the transfer line extract (equivalent to 0.8%) when PFBS was combusted. The analytical characterization of the PFBS used, does not indicate the presence of PFOS, and it seems unlikely that it would be formed through thermal rearrangement of PFBS in the pyroprobe. Also a small amount of PFOS (equivalent to 0.13%) was found in the transfer line extract of the transfer efficiency test. Additionally, a very small amount of PFBS (equivalent to 0.037%) was found in the second PUF in the two-PUF series of the transfer efficiency test. Again, PFOS is not listed as an impurity of the in its analytical characterization. PFBS is a possible thermal degradation product of the but if so, it is surprising that it is seen only in the second PUF in the series.

Table 5.7.2.3. Methanol Extraction Results for 2nd Transfer Efficiency Test

Sample	Extracts	PFOS (pg/μl)	PFOS (μg)	PFBS (pg/μl)	PFBS (μg)	(pg/μl)	(μg)
	1st	35.0	0.82	<25.2	<0.56	6.89	0.13
	2nd	<10.0	<0.24	<10.1	<0.22	<4.96	<0.097
PFBS	1st	233	5.5	805	18	<12.4	<0.25
	2nd	<10.0	<0.24	<10.1	<0.22	<4.96	<0.097
PFOS	1st	897	21	<63.0	<1.39	<12.4	<0.25
	2nd	<10.0	<0.24	<10.1	<0.22	<4.96	<0.097

Table 5.7.2.4. PUF Extraction Results for 2nd Transfer Efficiency Test

Sample	PUF Extracts	PFOS (pg/μl)	PFOS (μg)	PFBS (pg/μl)	PFBS (μg)	(pg/μl)	(μg)
	1st	<10.0	<0.25	<25.2	<0.23	<4.96	<0.10
	2nd	<10.0	<0.25	11.2	0.26	<4.96	<0.10
PFBS	1st	119	3.0	<25.2	<0.23	<4.96	<0.10
	2nd	<10.0	<0.25	<10.1	<0.23	<4.96	<0.10
PFOS	1st	<10.0	<0.25	<25.2	<0.23	<4.96	<0.10
	2nd	<10.0	<0.25	<10.1	<0.23	<4.96	<0.10

5.7.3. 3rd Transfer Efficiency Test

A 3rd transfer efficiency test was conducted to examine how much PFBS and PFOS can be transferred through the reactor/transfer line tubing and sampled by PUF cartridges if these samples were formed in the reactor. Two methanol extracts were obtained: 1) the heated reactor/transfer line tubing and 2) the unheated valve and associated transfer line tubing upstream of the PUF cartridges. Table 5.7.3.1 shows the net amount of gasified sample for each test. The experiments were carried out using both air and helium to compare the results. After a sample was placed in the reactor and the system was closed, the temperature of GC oven was increased to prevent the condensation of gasified sample. When the GC oven temperature reached 260°C, the furnace temperature was set to the temperature shown in Tables 5.7.3.2,

5.7.3.3, 5.7.3.4 and 5.7.3.5. The off-gas collection using PUF cartridges was initiated when the GC oven started heating.

Table 5.7.3.1. Net Amount of Gasified Sample for PUF Collection

Sample	Carrier Gas	Loaded Mass (mg)	Remained after Gasification (mg)	Net Amount of Gasified Sample (mg)
PFBS	Air	0.56	0.09	0.47
PFBS	He	0.59	0.20	0.39
PFOS	Air	0.48	0.00	0.48
PFOS	He	0.50	0.04	0.46

Tables 5.7.3.2, 5.7.3.3, 5.7.3.4, and 5.7.3.5 show flow rate profiles for PFBS and PFOS gasification under oxygen-rich and oxygen-deficient conditions.

Table 5.7.3.2. Flow Rate Profile for PUF Collection (PFBS Gasification with Air)

Time Period (sec)	Temperature Condition (°C)	Carrier Gas Used and Flow Rate (ml/min)	Total Volume (ml)	Sampled Volume[a] (ml)
0 – 421	GC Oven 25 → 260	Air 10.8	75.78	68.76
421 – 650	Furnace 99 → 575	Air 10.8	41.22	37.40
650 – 950	GC = 260, Furnace = 575	Air 10.8	54.00	49.00
950 – 1010	GC = 260, Furnace = 575	He 8.9	8.90	7.90
		Total (ml)	179.90	163.07

[a] Sampled volume for PUF collection.

Table 5.7.3.3. Flow Rate Profile for PUF Collection (PFBS Gasification with He)

Time Period (sec)	Temperature Condition (°C)	Carrier Gas Used and Flow Rate (ml/min)	Total Volume (ml)	Sampled Volume[a] (ml)
0 – 423	GC Oven 25 → 260	He 10.8	77.04	69.91
428 – 623	Furnace 110 → 550	He 10.8	35.10	31.85
623 – 983	GC = 260, Furnace = 550	He 10.8	64.80	58.80
		Total (ml)	176.94	160.56

[a] Sampled volume for PUF collection.

Table 5.7.3.4. Flow Rate Profile for PUF Collection (PFOS Gasification with Air)

Time Period (sec)	Temperature Condition (°C)	Carrier Gas Used and Flow Rate (ml/min)	Total Volume (ml)	Sampled Volume[a] (ml)
0 – 439	GC Oven 25 → 260	Air 10.7	78.29	70.97
439 – 637	Furnace 103 → 575	Air 10.7	35.31	32.01
637 – 937	GC = 260, Furnace = 575	Air 10.7	53.50	48.50
937 – 997	GC = 260, Furnace = 575	He 8.6	8.60	7.60
		Total (ml)	175.70	159.08

[a] Sampled volume for PUF collection.

Table 5.7.3.5. Flow Rate Profile for PUF Collection (PFOS Gasification with He)

Time Period (sec)	Temperature Condition (°C)	Carrier Gas Used and Flow Rate (ml/min)	Total Volume (ml)	Sampled Volume[a] (ml)
0 – 410	GC Oven 30 → 260	He 10.8	73.80	66.97
410 – 615	Furnace 140 → 575	He 10.8	36.90	33.48
615 – 975	GC = 260, Furnace = 575	He 10.8	64.80	58.80
		Total (ml)	175.50	159.25

[a] Sampled volume for PUF collection.

Tables 5.7.3.6 and 5.7.3.7 show the amount of recovered sample from the extracts and the PUF cartridges, respectively. The 3rd transfer efficiency test showed quite clearly that some measurable PFOS (3.8% air, 11% He) and PFBS (4.5% air, 1.7% He) could pass from the heated reactor, where it was volatilized in this test, to the PUFs. Larger amounts of PFOS (4.4% air, 30% He) and PFBS (3.3% air, 20% He) also accumulated in the reactor/transfer lines upstream of the PUF cartridges. The majority of the PFOS and PFBS accumulated in the portion of the transfer line heated to 260°C, suggesting that both of these compounds could condense, or were in a particulate form, at this temperature.

Table 5.7.3.6. Reactor/Valve Transfer Line Extraction Results

Sample	Gasification	Location	Extracts	PFOS (pg/μl)	PFOS (μg)	PFBS (pg/μl)	PFBS (μg)	(pg/μl)	(μg)
PFBS	Air	Reactor	1st	<10.0	<0.12	883	10	<4.96	<0.052
			2nd	<10.0	<0.12	12.8	0.15	<4.96	<0.052
		Valve	1st	<10.0	<0.035	3824	12	8.17	0.024
			2nd	<10.0	<0.035	69.9	0.23	<4.96	<0.014
	He	Reactor	1st	<10.0	<0.12	10484	124	<4.96	<0.052
			2nd	<10.0	<0.12	420	5.0	11.9	0.12
		Valve	1st	<10.0	<0.035	2510	8.2	<4.96	<0.014
			2nd	<10.0	<0.035	71.6	0.23	<4.96	<0.014
PFOS	Air	Reactor	1st	1908	24	81.4	0.96	<4.96	<0.52
			2nd	35.4	0.45	5.79	0.069	<4.96	<0.52
		Valve	1st	696	2.4	52.0	0.17	<4.96	<0.014
			2nd	22.8	0.079	<5.05	<0.016	<4.96	<0.014
	He	Reactor	1st	13530	171	237	2.8	<4.96	<0.052
			2nd	150	1.9	<5.05	<0.060	<4.96	<0.052
		Valve	1st	2218	7.7	47.4	0.15	<4.96	<0.014
			2nd	102	0.35	<5.05	<0.016	<4.96	<0.014

Table 5.7.3.7. PUF Extraction Results

Sample	Carrier Gas	Cartridge	PFOS (pg/μl)	PFOS (μg)	PFBS (pg/μl)	PFBS (μg)	(pg/μl)	(μg)
PFBS	He	1st	<10.0	<0.25	511	12	<4.96	<1.0
		2nd	<10.0	<0.25	<5.05	<0.12	<4.96	<1.0
	Air	1st	<10.0	<0.25	1255	29	<4.96	<1.0
		2nd	<10.0	<0.25	15.8	0.37	<4.96	<1.0
PFOS	He	1st	2330	58	37.4	0.87	<4.96	<0.10
		2nd	44	1.1	<5.05	<0.12	<4.96	<0.10
	Air	1st	997	25	14.7	0.34	<4.96	<1.0
		2nd	<10.0	<0.12	<5.05	<0.12	<4.96	<1.0

5.8. Sulfur Recovery Rate as SO_2, SOF_2, and SO_2F_2

Based on the in- and off-line GS/MS analyses, sulfur was found mainly as SO_2. No SOF_2 and SO_2F_2 was detected. Sulfur recovery rate as SO_2 using in-line GC/MS system was not quantitatively repeatable. This was due primarily to the low SO_2 peak resolution using the cryogenic focusing method at -60°C with a holding time of ca. 4 min. Because the SO_2 peaks using the off-line GC/MS system were much sharper than SO_2 peaks observed using in-line GC/MS, we decided to use off-line GC/MS analytical results to quantitatively analyze the sulfur recovery analysis as SO_2. The detailed operational procedures were described in Section 5.4.

Table 5.8.1 and Figure 5.8.1 show the calibration results. The sulfur recovery rate is reported on a molar basis. The formula obtained from this calibration was:

$$SO_2 \text{ (Mol)} = [\text{Area} + 494980] / [1.7997 \times 10^{14}]$$

Table 5.8.1. SO_2 Calibration Results Using PLOT Column

Conc. (ppm)	Mol. #	Area 1	Area 2	Area (Avg)
1000	4.09E-08	7191079	6980771	7085925
700	2.86E-08	4414365	4366705	4390535
400	1.63E-08	2304594	2295497	2300046
100	4.09E-09	425431	416699	421065

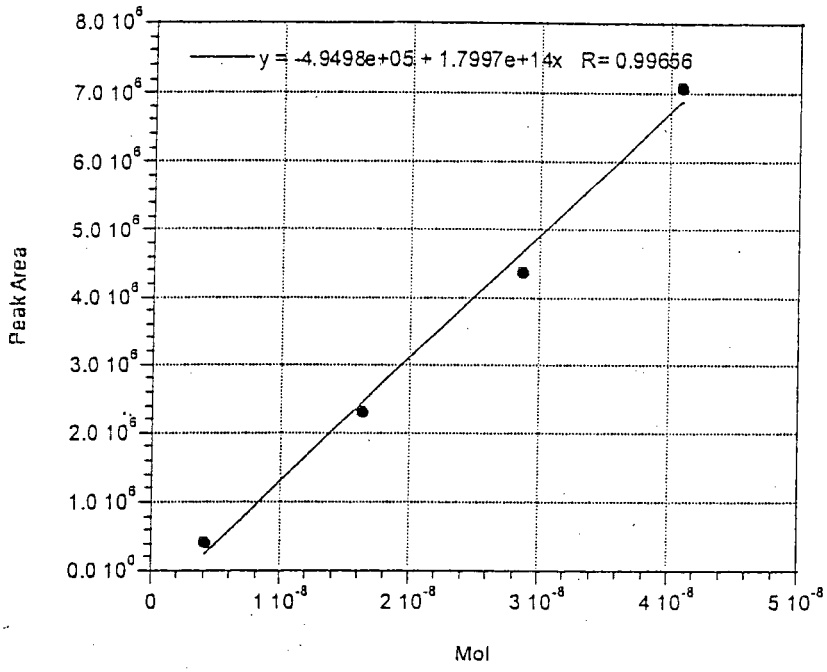

Figure 5.8.1. SO_2 Calibration Curve (Molar Number vs. Peak Area)

Prior to the sulfur recovery analysis as SO_2, a third SO_2 transfer efficiency test was conducted using the off-line analysis approach. Table 5.8.2 shows the results. Air was flowed through the reactor at 8.85 ml/min for 2 min. 30 sec. while the SO_2 standard was being injected and the off-gas was collected using a Tedlar bag. The average recovery rate was 75.6%. This is very similar to the recovery rates obtained from the in-line analysis, i.e. 83.7 and 76.4%, suggesting that the lack in 100% recovery is due to sample losses in the combustion system and not the sampling and analysis procedures.

Table 5.8.3 shows sulfur recovery rate as SO_2 for the seven compounds tested. The rate varies from 22.0 to 96.2 %. The last column shows sulfur recovery rate taking into account a transfer efficiency rate of 75.6%. The recovery rate as SO_2 for FC-1395 and is nearly 100% and that for FC-807A is greater than 100%. The recovery rate at 600°C was better than at 900°C for all compounds.

Table 5.8.2. Standard SO_2 Transfer Efficiency

Volume (ml)	Area	Calculated Mol. #	# of M ol. Used	Transfer Efficiency (%)
22.13	10591947	1.36E-06	1.63E-06	83.4
22.13	8515987	1.11E-06	1.63E-06	67.8
			Average	75.6

Table 5.8.3. Sulfur Recovery Rate as SO_2

Compound	Temp. (C)	Volume (ml)	Area	Calculated Mol. #	Gasified Mass (mg)	# of Mol. of Gasified Sample	Recovery Rate (%)	Recovery Rate after Efficiency Correction (%)
	600	34.64	8069545		2.10		48.4	64.0
	900	30.67	8136877		1.88		48.2	63.8
	600	53.93	4025040		2.78		36.0	47.6
	900	53.07	3508967		2.94		29.7	39.3
FC-1395	600	21.35	4159651	5.52E-07	0.52	7.15E-07	77.2	102.1
	900	19.55	3402701	4.23E-07	0.43	5.91E-07	71.6	94.7
FC-807A	600	21.81	6587251	8.58E-07	0.59	9.15E-07	93.8	124.0
	900	19.85	6354547	7.55E-07	0.53	8.22E-07	91.9	121.5
	600	21.71	10498604		0.52		78.9	104.4
	900	19.49	10366292		0.54		67.4	89.2
PFBS	600	21.89	4495370	6.07E-07	0.48	1.42E-06	42.8	56.6
	900	19.71	2000176	2.73E-07	0.42	1.24E-06	22.0	29.1
PFOS	600	22.07	2169830	3.27E-07	0.38	7.06E-07	46.3	61.2
	900	19.62	2676600	3.46E-07	0.50	9.29E-07	37.2	49.2

5.9. Extracted Ion Analysis

The following ions (69-CF_3, 119-C_2F_5, and 67-SOF) were extracted from the total ion chromatograms of all combustion tests (in-line and off-line GC/MS analyses) to analyze for the presence of perfluorinated and sulfonate-containing intermediates. The purpose of this analysis was to provide additional information regarding the potential formation of volatile fluorocarbons and volatile fluorinated oxysulfur compounds that were not identified in the GC/MS approach outlined in the previous sections. The analyses indicated that the 67 ions exist in negligible amounts thus indicating that all gas-phase sulfur compounds were indeed accounted in the analysis of the total ion chromatograms (as sulfur dioxide and carbon disulfide). This analysis further indicated that 69 and 119 ions were present in most if not all of the total ion chromatograms. Most notable here was the presence of these ions in the GC signals at short retention times, thus indicating that other volatile fluorocarbons were present that were not identified in the analysis of the total ion chromatograms.

Table 5.9.1 shows integrated 69 ion area counts from the in-line GC/MS analysis for the seven tests compounds when combusted at 600 and 900°C. The total areas at 900°C were smaller than those at 600°C by ratio ranging from 0.011 to 0.979. The analysis indicates that perfluorinated compounds were efficiently destroyed at 900°C for , FC-1395, FC-807A, and PFBS. Because large amounts of volatile fluorocarbons exist for combustion at both 600 and 900°C, there is only a slight difference of 69 ion peak area for both temperatures. No 69 ion was detected from the PFOS combustion chromatograms. Table 5.9.2 shows integrated 69 ion peak areas from the off-line GC/MS analysis for the seven test compounds. The results again show

that perfluorinated compounds were efficiently destroyed at 900°C with the exception of , which is again due to the large amounts of volatile fluorocarbons formed as intermediates.

Table 5.9.1. Integrated Peak Area of Extracted Ion (m/z = 69) (In-line GC/MS Data)

Compound	600°C	900°C	Peak Area Ratio (900°C/600°C)
	1.34E+07	1.05E+06	0.079
	4.38E+06	1.56E+06	0.357
FC-1395	1.23E+07	1.37E+05	0.011
FC-807A	1.12E+07	1.80E+06	0.160
	1.85E+07	1.82E+07	0.979
PFBS	1.27E+07	1.64E+05	0.013
PFOS	0.00E+00	0.00E+00	---

Table 5.9.2. Integrated Peak Area of Extracted Ion (m/z = 69) (Off-line GC/MS)

Compound	600°C	900°C	Peak Area Ratio (900°C/600°C)
	5.69E+06	3.43E+05	0.06
	2.96E+05	0.00E+00	0.00
FC-1395	3.84E+05	0.00E+00	0.00
FC-807A	8.11E+05	0.00E+00	0.00
	3.31E+06	1.94E+06	0.584
PFBS	3.83E+05	0.00E+00	0.00
PFOS	0.00E+00	0.00E+00	---

During the analysis of the off-line samples, we collected hydrogen flame ionization detector (HFID) as well as mass spectral data. Due to the suspect results from the extracted ion analysis of the total ion chromatograms generated from PFOS combustion, the FID data for PFBS, and PFOS were analyzed in an attempt to provide an indication of the potential formation of volatile fluorocarbons from the combustion of PFOS as related to the other active ingredients. This analysis does not give quantifiable results, but does have the potential to show the existence of fluorocarbons in the byproducts from PFOS combustion.

Figure 5.9.1 shows the total ion chromatogram and the corresponding HFID signal for off-line GC/MS analysis at 600°C. A HFID peak appears with same retention time as the "air" peak for the total ion chromatogram. Since the FID does not respond to the molecular constituents in air (N_2, O_2, Ar, CO_2) but does respond to fluorocarbons, it is apparent that volatile fluorocarbons are eluting from the GC column simultaneously with the air constituents. Mass spectral ions corresponding to volatile fluorinated compounds, including CF_2H-51, SOF-67, CF_3-69, CF_2CF_2H-101, and C_2F_5-119, were extracted from the total ion chromatogram and are shown in Figure 5.9.2 along with the HFID signal. The results indicate that the HFID peak at a retention time of 0.8 min. corresponds to a mass spectral signal that contains the following fluorocarbon ions: 51, 69, and 119. The 51 ion occurs near the tail of the FID signal while the 69 and 119 ions occur near the peak of the FID signal. Likely candidates that can be attributed to

the 51 and 69 ions are tri- and tetrafluoromethane. Likely candidates for the 119 ion are penta or hexafluoroethane. Pentafluoroethane is detected at longer retention times and also contains a strong 101 ion that is not present in the unknown peak. It is plausible that hexafluoroethane would elute earlier than pentafluoroethane due to its lower boiling point. Thus, the most probable candidates that correspond to the HFID signal at 0.8 min. are tri- and tetrafluoromethane and/or hexafluoroethane.

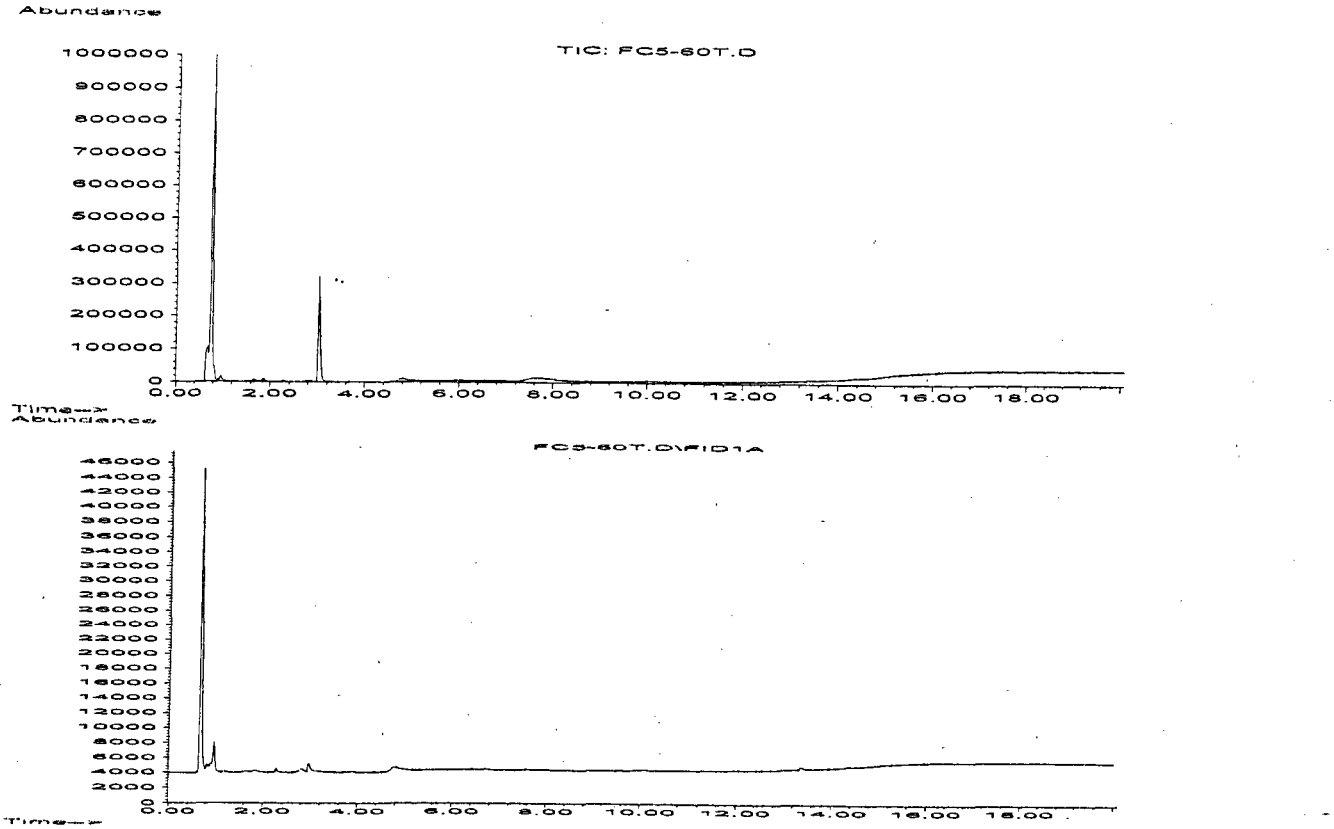

Figure 5.9.1. Total Ion Chromatogram and Corresponding HFID Signal for Combustion of at 600°C (off-line sample)

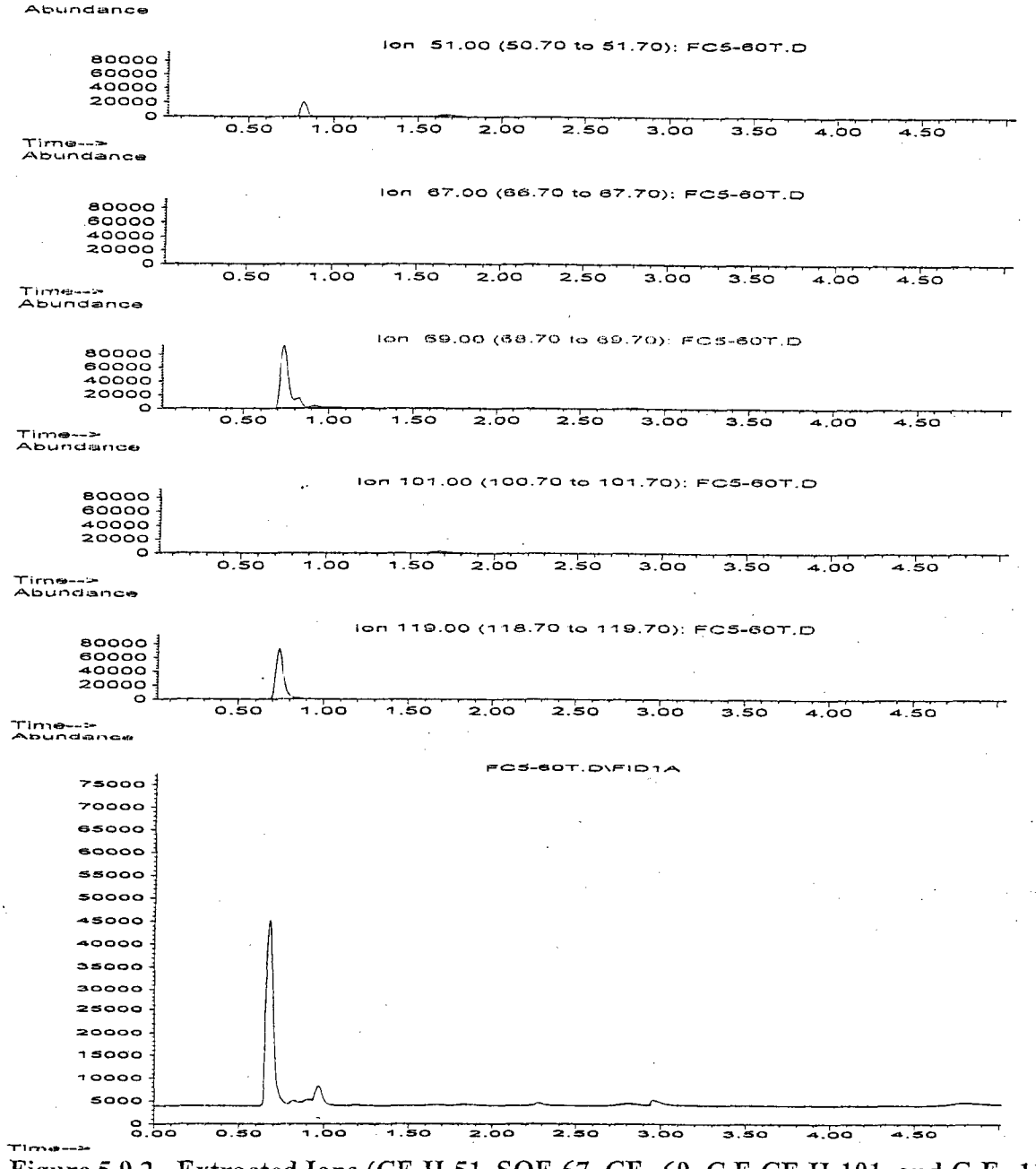

Figure 5.9.2. Extracted Ions (CF_2H-51, SOF-67, CF_3-69, C.F_2CF_2H-101, and C_2F_5-119) and Corresponding HFID Signal for Combustion of at 600°C (off-line sample)

Figure 5.9.3 and 5.9.4 show the HFID signal for PFBS and PFOS combustion at 600°C, respectively, and the integrated HFID peak areas for PFBS, and PFOS are shown in Table 5.9.3. The peak for PFOS shows the largest area with the smallest amount of gasified sample. The HFID signal for PFOS combustion at 900°C is also shown in Figure 5.9.5. The peak is negligible compared to one at 600°C, thus indicating nearly complete destruction of fluorinated compounds under these conditions.

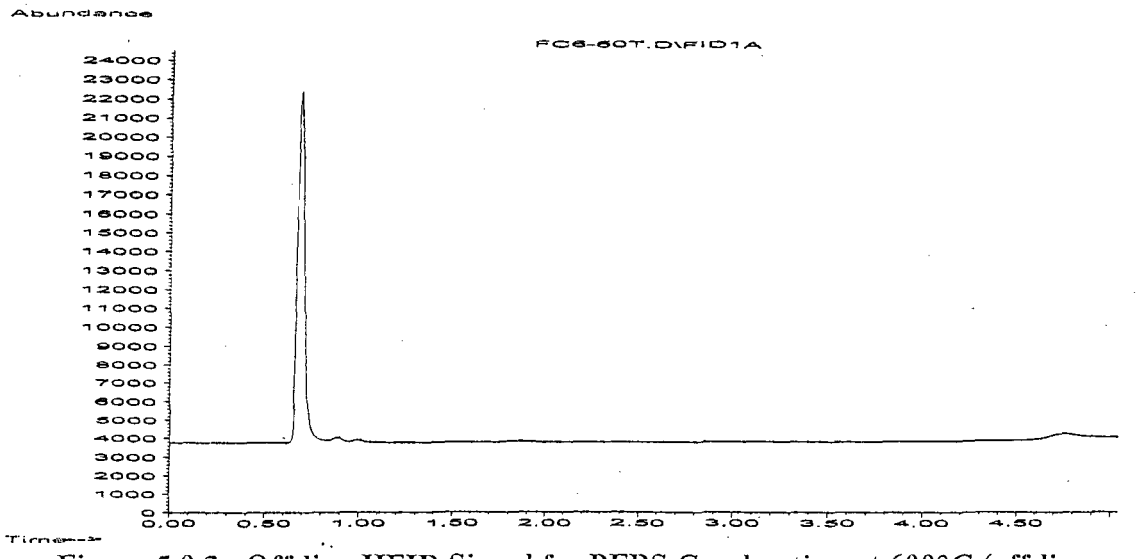

Figure 5.9.3. Off-line HFID Signal for PFBS Combustion at 600°C (off-line sample)

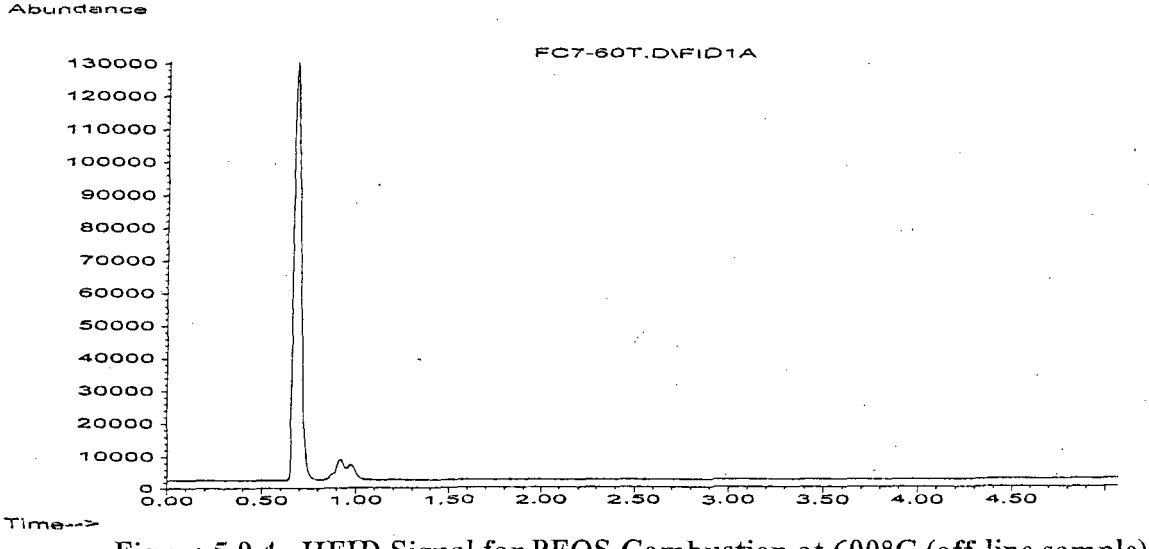

Figure 5.9.4. HFID Signal for PFOS Combustion at 600°C (off-line sample)

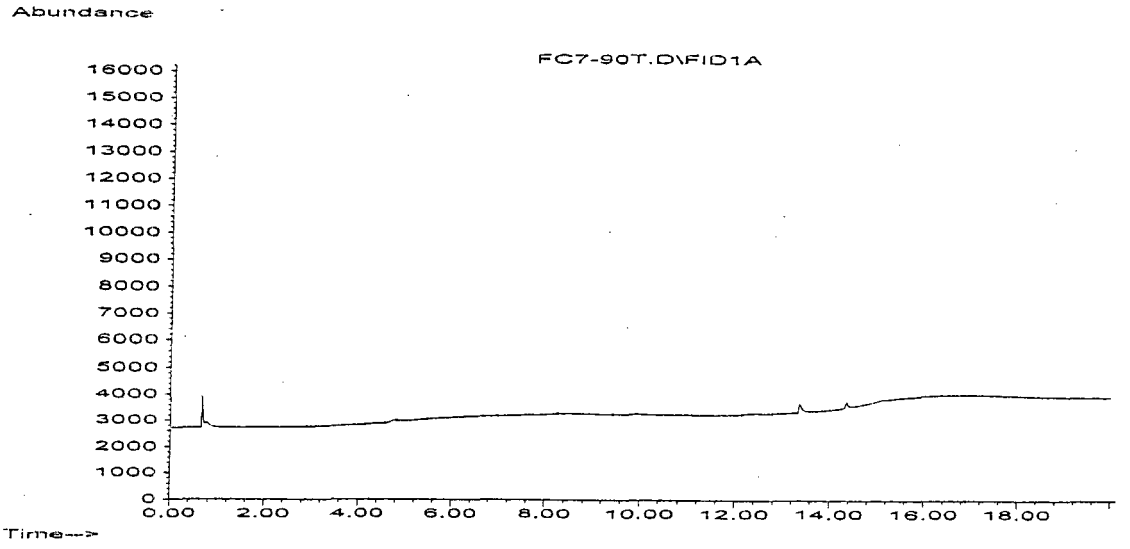

Figure 5.9.5. HFID Signal for PFOS at 900°C (off-line sample)

Table 5.9.3. Integrated HFID Peak Area at 600°C

Sample	Peak Area	Net Amount of Gasified Sample (mg)
	1190193	0.52
PFBS	512226	0.48
PFOS	3547614	0.38

6. Discussion

The motivation of this study was to assess the incinerability of perfluoroalkyl sulfonate compounds and polymers that contain these active ingredients. A laboratory-scale study roughly simulating a full-scale hazardous or municipal waste incinerator was envisioned in the phase I test protocol. Based on prior experience with halogenated compounds, we initially planned to use relatively modest conditions in the primary combustion zone (ca. 400°C) to gasify the materials with more severe high-temperature (600 – 900°C), oxidative conditions applying to the secondary combustion zone. TGAs of the active ingredients indicated that higher temperatures (~ 600°C) were necessary to gasify these unique materials. The sponsor also requested that the experiment be designed to detect low-level (0.1%) transformation to perfluoroalkyl sulfonates in the exhaust gases from the fluorinated portions of the test compounds. The combination of these factors necessitated the use of large amounts of material (milligram quantities) and high-temperature, long duration exposures (ca. 1250°C, 40 sec) in a specially designed pyroprobe to fully gasify the material. These conditions, while representing quite severe conditions in the primary zone of an incinerator, e.g., a rotary kiln, are representative of the range of conditions that occur in a full-scale system. As such, the approach employed in the laboratory-scale combustion study described in the phase III test protocol is a reasonable extrapolation of a full-scale hazardous or municipal waste incineration study of perfluoroalkyl sulfonates and polymers that contain these active ingredients.

Combustion tests were completed for seven fluorinated alkyl sulfonyl hydrocarbons: , FC-1395, FC-807A, , $C_4F_9SO_3^-K^+$ (PFBS), and $C_8F_{17}SO_3^-K^+$ (PFOS) as requested by the sponsor. In-line and off-line GC/MS analyses, reactor effluent sample collection using PUF cartridges followed by LC-MS analysis, and chemical extraction of various transfer lines throughout the reactor system including the reactor itself followed LC-MS analysis were conducted to investigate the following: 1) the extent of conversion of the active ingredients, 2) the formation of fluorinated intermediate organic products, and 3) the extent of conversion of the sulfur to sulfur oxides.

There was no indication that perfluoroalkyl sulfonate compounds PFBS, and PFOS) were generated from FC-1395, and FC-807A combustion. No quantifiable amount of perfluoroalkyl sulfonyl compounds (ca. 10 ng/ml) was detectable at a detection limit of ca. 10 ng/ml. Combustion of also showed no quantifiable amount of perfluoroalkyl sulfonyl compounds including itself. During PFBS combustion, small amounts of PFBS were detected in the reactor/transfer lines and the PUF sample cartridges, specifically, 0.22% of gasified sample in the reactor/transfer line system, 0.6% in the PUF cartridges at 600°C, and 1.1% in the PUF cartridges at 900°C. Similarly, during PFOS combustion, small amounts of PFOS were detected in the reactor/transfer line system and the PUF sample cartridges, specifically, 0.04% of gasified sample in the reactor/transfer line system, less than 0.4% in the PUF cartridges at 600°C, and 0.05% in the PUF cartridges at 900°C. The correction for this fraction is too complicated and ambiguous to make accurately because of the complexity of the flow scheme, mainly due to changes in both concentration and split ratio with time. If corrected, these recoveries would likely be 10 to 15 percent higher.

Minor evidence of cross contamination was found from several LC/MS analyses. The cross-contamination was only observed in tests of the active ingredients and do not invalidate the earlier combustion tests of the fluorinated polymers. The contamination sources are likely the pyroprobe and the methanol extraction tubing (separate from the combustion apparatus). All reactor/transfer lines were replaced with each subsequent combustion test. Both pyroprobe and methanol extraction tubing were cleaned following each combustion test. They were not replaced during the tests.

To validate the experimental results pertaining to the sampling and analysis of PFOS, PFBS, and where in many instances the analytical results were below the level of quantitation, a series of transfer efficiency tests were conducted. The goals of the transport (or transfer) efficiency tests were: 1) to see if parent compounds and reference compounds, particularly those that were potential thermal transformation products, e.g., PFOS and PFBS, could pass through the combustion system under nondestructive conditions and reach the PUF cartridges and, 2) to determine recovery efficiencies and analytical detection limits.

In the 1st transfer efficiency test where the ability of the combustion system to transport all three active ingredients was assessed, analysis of the PUF cartridges indicated the lack of any detectable material. This result indicated that the sample was either thermally destroyed in the pyroprobe chamber (1250°C) or the gasified sample condensed in the pyroprobe/reactor transfer lines and never reached the PUF sample cartridge. Based on the results of 1st transfer efficiency test, a 2nd transfer efficiency test was conducted to investigate the latter possibility. In these tests, substantial amounts, 3.4% of PFOS gasified and 2.6% of PFBS gasified, were indeed found in the pyroprobe/transfer line extracts. However, once again, analysis of the PUF cartridges positioned downstream of the pyroprobe/transfer line were negative. The 2nd test showed that measurable amounts of PFOS and PFBS survive pyrolytic conditions in the pyroprobe and the heated (260°C) transfer lines. The question now was how much PFBS or PFOS was transferred through the reactor/transfer line tubing and sampled by PUF cartridges if these materials were formed in the combustion chamber. A 3rd transfer efficiency test was then conducted to address this question. In this test, PFOS or PFBS were placed in the combustion chamber and not into the pyroprobe. The temperature of the combustion chamber and transfer line system was then heated to 260°C. This is the temperature of the transfer lines within the oven during the actual combustion tests. At this temperature, TGAs indicated there would be no PFOS volatilization, so there would be no PFOS movement through the system (The TGAs were conducted at UDRI during the phase I protocol development). The combustion chamber was then heated to 600°C while the transfer lines remained as 260°C. When the combustion chamber was heated, some of the PFOS or PFBS must have been entrained into the gas stream, and a larger proportion was probably destroyed. Nevertheless, a substantial portion of the PFOS and PFBS was transported through the transfer lines to the PUFs where it was detected. PFOS and PFBS were also found in the transfer lines. Specifically, results showed that measurable PFOS (3.8% air, 11% He) and PFBS (4.5% air, 1.7% He) passed from the combustion chamber to the PUF sampling cartridges. Results also showed that larger amounts of PFOS (4.4% air, 30% He) and PFBS (3.3% air, 20% He) accumulated in the reactor/transfer lines upstream of the PUF cartridges. These results demonstrated that if PFOS or PFBS were formed in the combustion chamber, they would be detected in the PUFs. Therefore, when no PFOS or PFBS was observed in the transfer lines or PUFs downstream of the combustion chamber in tests of potential PFOS or PFBS precursors,

one could conclude that there must have been very little, if any, PFOS or PFBS formed during combustion.

A sulfur mass balance was attempted based on the premise that all of the sulfur in the samples would be oxidized to SO_2, SOF_2, and SO_2F_2 under high-temperature oxidative conditions. The GC/MS analyses indicated that the sulfur was recovered as either SO_2 or carbon disulfide, CS_2. A large SO_2 peak was observed for all of species and a much smaller CS_2 peak was observed for FC-1395, FC-807A, . Recovery rates were variable. Nearly 100% sulfur recovery was obtained from FC-1395 and . Greater than 100% of recovery rate was obtained from FC-807A. Recovery rates for the other compounds were typically less than 60%. There are two potential sources of error in the sulfur mass balance. The most likely is the condensation of the active ingredients and their primary degradation products in the pyroprobe and the pyroprobe/reactor transfer lines. The sulfur mass balance does not take into account this potential source of sulfur in the system as these lines were not extracted and analyzed for sulfur compounds. Another potential source of error is the lack of complete quantitative transport of the SO_2. Three SO_2 transport efficiency tests yielded an efficiency of 78.6±4 %. The SO_2 transport efficiency was accounted for in the sulfur mass balance. The high repeatability of these recovery tests suggests that this source of error is small compared to condensation of the active ingredients and their primary degradation products.

GC/MS analysis of the reactor effluent was conducted to assess the formation of combustion intermediates, i.e., products of incomplete combustion. The most abundant combustion byproduct was benzene. Benzene was observed for the all of the samples except PFOS. Heavier aromatic hydrocarbons were only observed in the two cases where fuel was not supplied with the fluorocarbon sample due to constraints on the reaction stoichiometry. In these cases, , commonly observed high molecular weight aromatic hydrocarbons included styrene, benzaldehyde, benzonitrile, phenol, and naphthalene. The combustion tests were performed under oxygen-rich conditions. The excess air ranged approximately from 50% (for combustion) to 140% (for FC-807A combustion). However, during sample gasification, it is plausible that an excess amount of sample was introduced into the reactor due to thermal expansion and a fuel-rich condition was created and might be responsible for the formation of light polycyclic aromatic hydrocarbons (PAHs). This is roughly analogous to fuel-rich conditions that sometimes occur in full-scale systems due to the uneven loading of solid fuel into the primary combustion chamber and the lack of control of the gasification process. Besides relatively light hydrocarbons, several fluorinated compounds were also observed. The intermediate in highest concentration at 600°C was a C_1 fluorocarbon alkane, most likely tri- or tetrafluoromethane. This compound or compounds was observed from the combustion of each fluorochemical. At 900°C, the concentration of this compound was much lower in comparison with the 600°C results. The nature of this byproduct and its thermal stability is consistent with other tests we have conducted on fluorinated samples that show that perfluorinated alkanes are stable intermediates and require temperatures in the secondary combustion zone in excess of 900°C for high levels of destruction (Ciba Special Chemicals Corp., 2002). Pentafluoroethane and 1,1- or 1,2-difluoroethene were also observed in several tests, i.e. , FC-1395, PFBS, and PFOS combustion. The formation of perfluoroalkanes and alkenes was not unexpected and is consistent with the molecular structure of the starting materials, particularly the active ingredients, where a C_4 or C_8 saturated fluorocarbon chain is present. There was no

evidence to suggest that fluorinated acids were significant combustion products. Fluorinated acids have been observed by GC/MS analysis in combustion studies of other fluorinated materials (Ciba Special Chemicals Corp., 2002), but were not observed in this study. Fluorinated aromatics, i.e., mono-, di-, and trifluorobenzene, were observed from most of the samples in relatively low yields. These compounds are also stable intermediates and were not unexpected. Projected yields of fluorinated aromatics were low compared to the nonfluorinated aromatic hydrocarbons. There was no evidence of molecular growth of the fluorinated aromatic compounds. There was no evidence to suggest that polyfluorinated biphenyls or dioxins could have formed under these conditions.

Further analytical testing was conducted to verify that the following compounds, potential precursors to PFOS and PFBS, were not formed during the combustion tests: POSF, PBSF, $C_4F_9SO_2NH_2$, $C_8F_{17}SO_2NH_2$. In all cases, there was no evidence that these precursors formed during the combustion of the seven samples. Further examination of the total ion chromatograms for the SOF ion also indicated the lack of formation of secondary amine precursors, i.e., N-MeFOSE alcohol ($C_8F_{17}SO_2N(CH_3)C_2H_4OH$), and , during the combustion of the seven samples. Fluoro-organic sulfur compounds were not observed in the effluent indicating that the C-S bond in the fluorinated polymers was completed destroyed. This was also likely the case for the active ingredients, PFOS, PFBS, and In these latter studies, a small amount of undestroyed starting material was observed in the LC/MS analyses. It is unlikely that these starting materials were reformed during the combustion process due to the presence of large amounts of methane as the fuel for the combustion process. The presence of excess methane fuel relative to fluorochemical product results in significant concentrations of H atoms that efficiently scavenge F atoms as HF and prevent the reformation of long perfluoroalkyl chains. The hydrocarbon fuel to fluorochemical ratio will likely be even higher under actual incineration conditions, further limiting the reformation of perfluoroalkyl chains. Perfluorinated alkanes, necessary building blocks to the formation of precursors to PFOS and PFBS, were limited to C_1 and C_2 compounds, further indicating that reformation of PFOS, PFBS, requiring C_4 and C_8 perfluoroalkyl chains, did not occur in the combustion system.

7. Conclusions

The data presented herein clearly show that incineration of FC-1395 and FC-807A does not release perfluorinated alkyl sulfonates to the environment. This conclusion is based mainly on the LC/MS measurements, but was substantiated by the extracted ion analysis that showed negligible 67-SOF ion indicating negligible amounts of volatile sulfonate-containing degradation products. Sulfur recoveries varied from 40 to 120%, depending on the fluorocarbon or fluorocarbon polymer combusted. The dominant sink for sulfur was SO_2. GC/MS analysis of perfluorinated alkyl sulfonate precursors indicated that such precursors were not present in the reactor effluent. This finding is consistent with the LC/MS measurements, and strongly suggests that the C-S bond was completely destroyed (and did not reform) in the combustion tests.

Several fluorinated organic intermediates were observed in the reactor effluent. These compounds were limited to fluorinated alkanes, fluorinated alkenes, and fluorinated aromatics. Higher molecular weight fluorinated polycyclic aromatic hydrocarbons were not observed. Recent combustion tests at UDRI with related highly fluorinated polymers (Ciba Specialty Chemicals, 2002) indicate that secondary chamber temperatures of ca. 950°C are required to achieve destruction efficiencies of 99.99%. Other tests with C_1-C_4 fluorinated alkanes indicate that temperatures between 1040 to 1050°C are required to achieve similar destruction efficiencies.

The data from this laboratory-scale incineration study indicates that properly operating full-scale incineration systems can adequately dispose of these unique materials. Incineration of these fluorinated compounds is not likely to be a significant source of perfluorinated alkyl sulfonates into the environment. Fluorinated organic intermediates are also unlikely to be emitted from these facilities.

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Appendix 1

Timeline and Dates of Testing

Project Time Line

Phase I	March 2001 – October 2001
Phase II	February 2002
Phase III	March 2002 – September 2002

Combustion Test Schedule - 2002

Date	Description
2/1, 2/4, 2/7,2/15, 2/18, 2/19, 2/24	Standard sample calibration
3/19 – 7/29	Combustion test system and method development
7/30	PFOS and PFBS extraction
8/2	Heated blank extraction before combustion test
8/5	combustion test
8/7	combustion test
8/8, 8/9	FC-1395 combustion test
8/19, 8/20	FC-807A combustion test
8/21	combustion test
8/22	PFBS combustion test
8/23, 8/26	PFOS combustion test
8/27	Heated blank extraction after combustion test
8/28	PFBS, and PFOS transfer efficiency test
8/30	2nd PFBS, and PFOS transfer efficiency test
9/3 – 9/5	Off-line GC/MS SO_2 calibration
9/6	Non-heated blank extraction
9/18 – 9/20	3rd PFBS, and PFOS transfer efficiency test

Appendix 2

Phase II Final Report and Raw Data

August 1, 2002

3M Phase II Final Report: Laboratory-Scale Thermal Degradation of Perfluoroalkyl Sulfonates and Perfluoroalkyl Sulfonamides

Prepared by:
Environmental Sciences and Engineering Group
University of Dayton Research Institute

Summary

Calibration curves and detection limits for SO_2, SOF_2, SO_2F_2, POSF, PBSF, and C_3F_6 (hexafluoropropene (HFP)) have been established. The transport efficiency through the UDRI thermal instrumentation system for each compound was also examined. This report describes experimental setup, operating procedure, analytical methods and their results. The calibration plots, linear fit equations, detection limits, and transport efficiency are provided in this report. Verification that C_4 and C_8 perfluoroalkyl sulfonates can be gasified and transported through the system will be performed following the completion of the phase III tests. This decision was made based on the potential contamination of the system had the transport tests been done prior to the phase III combustion study. HFP was selected as the surrogate volatile fluorocarbon due to the lack of availability of CF_4 and CF_3H from gas suppliers.

Experimental Setup

Six standards (SO_2, SOF_2, SO_2F_2, POSF, PBSF, and HFP) were injected through the STDS reactor configuration that will be used for the Phase III combustion test. The same samples were also injected directly into the GC/MS system and compared with the earlier tests to derive the transport efficiency for each material. Figure 1 shows a schematic diagram of reactor and in-line GC/MS system that was used for the Phase II study.

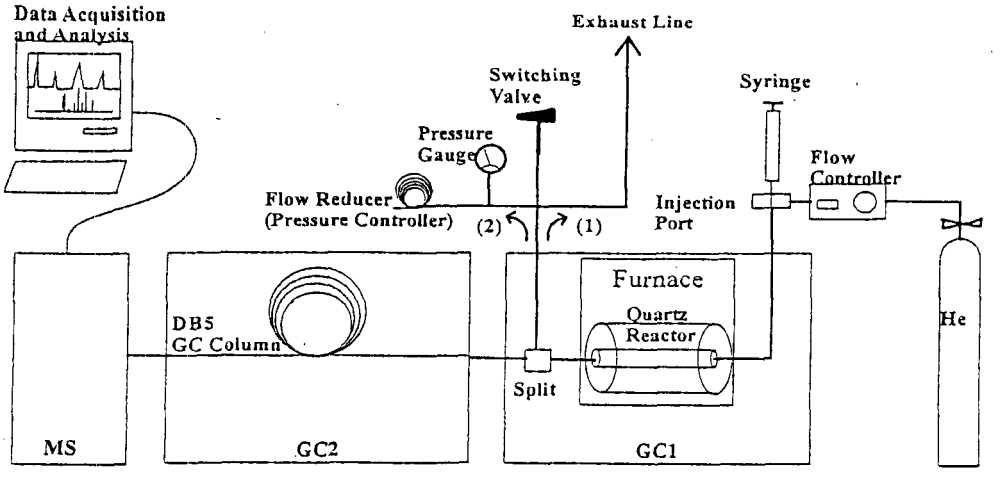

Figure 1. Schematic Diagram of Experimental Setup for the Phase II Study.

The system consists of two GCs, the first GC (GC1 in Figure 1) was used to maintain reactor and transfer line at 260°C to transport samples efficiently and the second GC (GC2 in Figure 1) was used for sample analysis. The furnace in GC1 was also maintained at a temperature of 260°C. Helium (He) was used as carrier flow and flow was set as 21 ± 1 ml/min using a differential flow controller (Porter Instruments). A flow splitter was installed between reactor and GC column to vent excess gas. A 21 ml/min flow rate was used to define a residence time of 1 sec in the combustion reactor. The combustion reactor used in this study (and the Phase III combustion test) is 4 mm × 6 mm (i.d.×o.d.) with an effective length of 5 cm. While the sample was being collected, the switching valve was opened toward exhaust line ((1) position in Figure 1. The valve was then switched to (2) position to pressurize GC column when sample analysis was started. The pressure was maintained at approximately 6 psi during sample analysis and the pressure was monitored using a pressure gauge. The GC/MS system used in Phase II analysis was a Hewlett Packard 5890A/5970B incorporating a DB-5 MS capillary column (30 m length, 0.25 mm i.d., Agilent Technologies, Inc.).

All samples except PBSF were diluted in helium (Research Grade, Air Products, Inc.) to establish calibration curves and detection limits. PBSF, which is a liquid phase at room temperature, was diluted in dichloromethane (99.9% HPLC grade from Aldrich, Inc.). The amount of sample injected was 1 ml for gas-phase samples (SO_2, SO_2F, SO_2F_2, POSF, and HFP) and 1 µl for liquid-phase sample (PBSF). Measurements were performed in duplicate for each sample and concentration.

Operating Procedure

Calibration

Prior to sample injection, the switching valve was set to (1) position to vent excess gas and the second GC oven (GC2) was held at –60°C. After sample injection, the flow was vented for approximately 1 min. to purge the sample from the reactor/transport system. The system was then pressurized by turning the switching valve to the (2) position, and the GC oven temperature programming was started. The GC oven was initially held at –60°C for 1 min., heated to 50°C at 10°C/min. and held for 1 min. The GC was heated to 250°C for 10 min after each analysis to flush out any residual material from the column. The MS was auto-tuned with perfluoro-tributylamine (PFTBA) and operated at EMV (2000V) in the scanning mode sweeping from 45 to 550 AMU.

Direct Injection

All conditions, GC oven temperature programming, total flow, split ratio, injection port temperature, and column pressure, were set at the same condition that was used for the calibration study. The temperature programming was started immediately after sample injection.

Results

Calibration

In most cases, calibrations were made based on four even interval concentrations for each sample. The detection limit was determined using a similar approach to EPA's detection limit criteria for identifying an unknown (Method 8260B page 23 – 24). In our approach, the masses of the most abundant ions comprised the reference mass spectra. We then chose the most abundant ion (target ion) and major ions whose intensities are greater than ca. 20% of the target ion. The detection limit was then specified as the lowest concentration that has the target ions and all of the major ions whose relative intensity agrees with the reference spectra within ca. ± 20%.

For example, Figure 19 and 20 in the Appendix illustrate the total ion chromatogram and mass spectra for SO_2F_2 (10,049 ppm). The m/z = 83 ion is the most abundant ion (target ion) and m/z = 48, 67, and 102 are the major ions (m/z will not be shown thereafter). The ions of 102, 83, 67, and 48 correspond to SO_2F_2, SO_2F, SOF, and SO, respectively and it is reasonable to choose these ions to quantify SO_2F_2. Figures 24 and 25 in the Appendix show the total ion chromatogram and mass spectra for a concentration of 20.1 ppm. The mass spectra still contain the target ion and the 3 major ions and their relative abundance agrees with the reference spectra (Fig. 20). Figures 26 and 27 show the total ion chromatogram and mass spectra for a concentration of 4.0 ppm. The 102 ion is not present at this concentration. Therefore, the detection limit for SO_2F_2 was determined as 20.1 ppm. Similar analysis was conducted for all of standards and the results are briefly discussed below.

Figures 2 to 7 show calibration plots for SO_2, SOF_2, SO_2F_2, POSF, PBSF, and HFP, respectively. The linear fit equations for each sample, their linear correlation coefficients (R) and detection limits are tabulated in Table 1.

Table I Linear Fit Equations and Detection Limits

Sample Name	Linear Fit (Y: peak area, X: concentration (ppm))	R	Detection Limit (ppm)
SO_2	Y = 5.8813E3* X - 3.8541E5	0.9971	78.5
SOF_2	Y = 8.3335E3* X - 7.0267E4	0.99941	30.3
SO_2F_2	Y = 1.0331E4*X + 1.8273E6	0.99708	20.1
POSF	Y = 1.0423E5*X – 8.4043E5	1.0	14.1
PBSF	Y = 1.564E5*X + 1.338E6	0.998	10.0
HFP	Y = 1.4975E4*X - 2.8253E6	0.9997	3.9

The linear fit for each calibration shows reasonable high correlation coefficients. Because only 2 concentrations could be measured above the detection limit for POSF, the R value is 1.0. Based on the linear fit equation, the detection limit for HFP is 189 ppm. However, the detection limit analysis described above indicates a much smaller value (3.9 ppm). This is due to non-linear GC/MS response throughout the concentration range examined.

The concentration range used to obtain the SO_2 calibration curve was 1570 to 157 ppm. The detection limit was determined as 78.5 ppm. Figure 10 in the Appendix shows the mass spectra for SO_2 (1570 ppm). The ions of 48 (SO) and 64 (SO_2) were chosen as target ion and major ion, respectively. The ion of 64 was not evident at a concentration of 15.7 ppm. The detection limit was thus determined as 78.5 ppm.

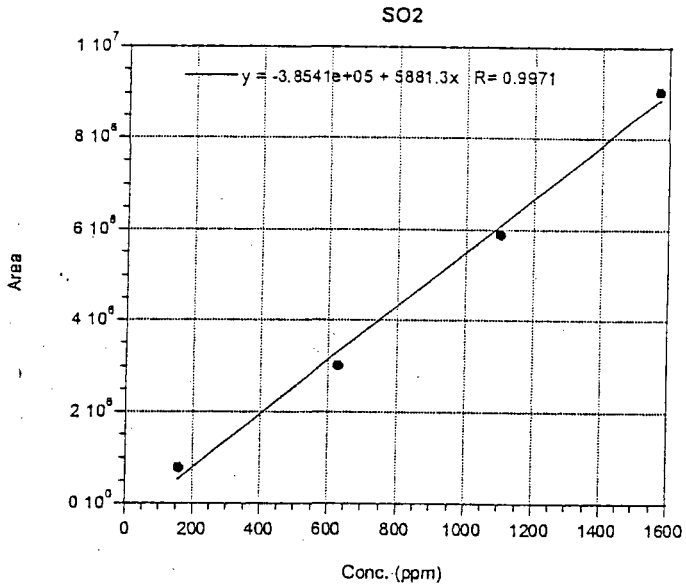

Figure 2. Calibration Plot for SO_2

The concentration range used to obtain the SOF_2 calibration was 3034 to 303.4 ppm. Figure 9 in the Appendix shows the mass spectra for SOF_2. The ion of 67 (SOF) was chosen as target ion and the ions of 86 (SOF_2) and 48 (SO) were chosen as major ions. All ions exist at a concentration of 30.3 ppm. At 6.1 ppm, there was no GC/MS response to the sample. Therefore, the detection limit was determined as 30.3 ppm.

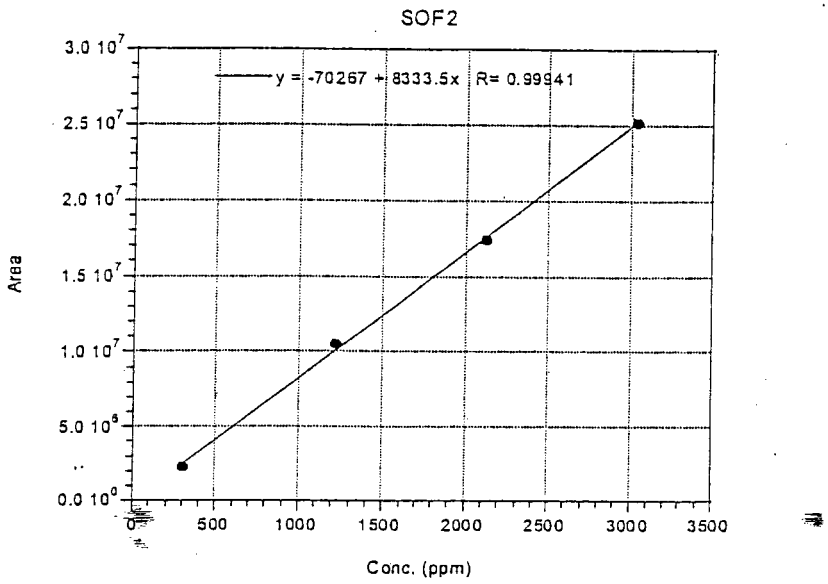

Figure 3. Calibration Plot for SOF_2

The concentration range used to obtain SO_2F_2 calibration was 7034.3 to 100.5 ppm. The detection limit was determined as 20.1 ppm as discussed above.

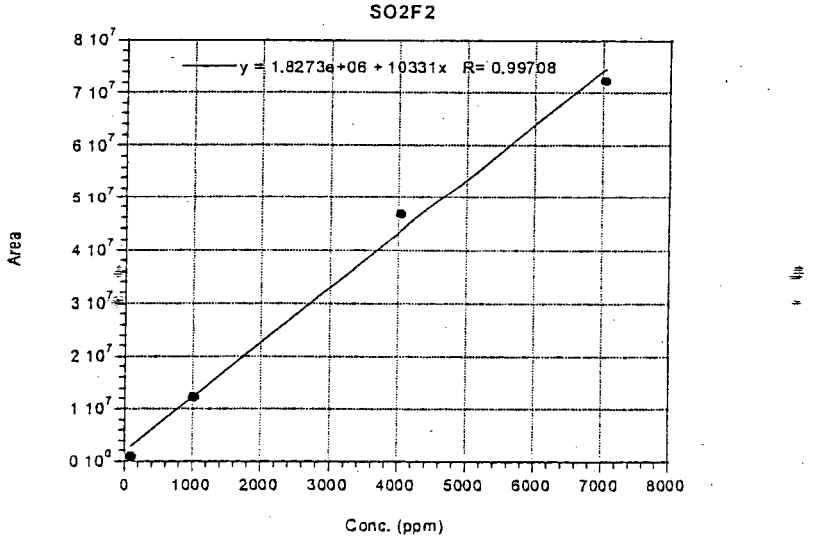

Figure 4. Calibration Plot for SO_2F_2

The concentrations used to obtain the most accurate POSF calibration were 20.1 and 14.1 ppm. This limited range is due to the low concentration of the standard provided by 3M and the tight detection limit criteria. Figure 29 in the Appendix shows the mass spectra for POSF (20.1 ppm). The 69 ion (CF_3) was chosen as target ion and 67 (SOF), 100, 119 (C_2F_5), 131 (C_3F_5), and 169

(C_3F_7) were chosen as the major ions. The 100 and 131 ions were not present at a concentration of 8 ppm (Fig.33), and the detection limit was determined as 14.1 ppm.

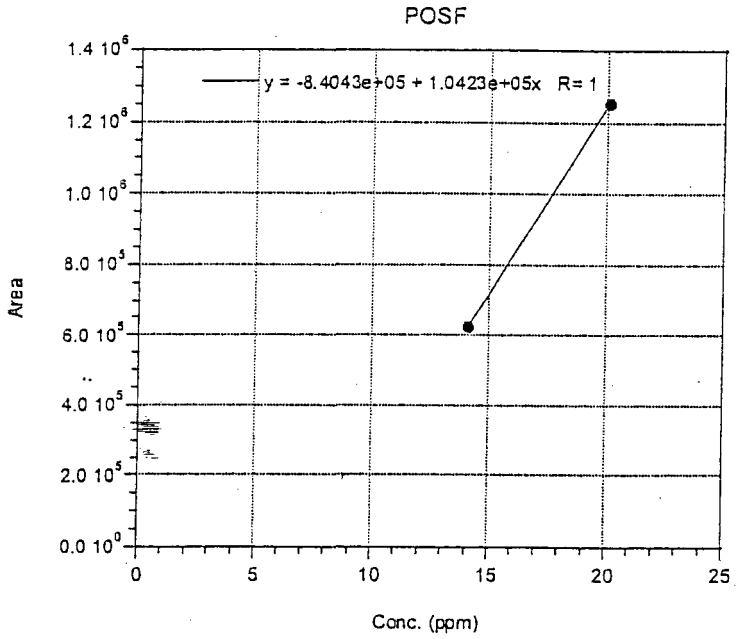

Figure 5. Calibration Plot for POSF

The concentration range used to obtain the PBSF calibration was 1000 to 100 ppm. Figure 35 in the Appendix shows mass spectra for PBSF (1000 ppm). The 69 ion (CF_3) was chosen as target ion and 67 (SOF), 100, and 131 (C_3F_5) were chosen as major ions. The 100 and 131 ions were not present at a concentration of 5 ppm (Fig.42). The detection limit was thus determined as 10.0 ppm.

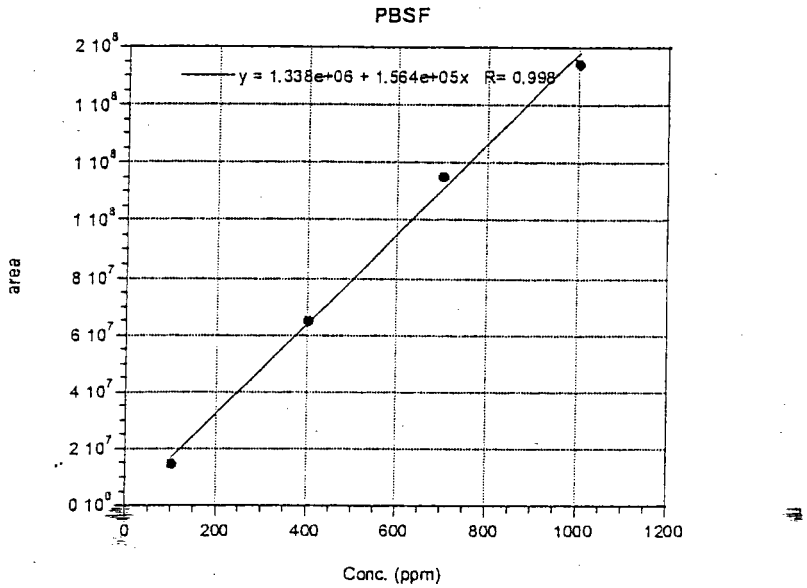

Figure 6. Calibration Plot for PBSF

The concentration range used to obtain the HFP calibration was 10,000 to 1,000 ppm. Figure 44 in the Appendix shows mass spectra for HFP (10,000 ppm). The 69 ion (CF_3) was chosen as target ion and 50 (CF_2), 81 (C_2F_3), 100, 131 (C_3F_5), and 150 were chosen as major ions. The ion of 81 was not present at a concentration of 1.9 ppm (Fig. 51). The detection limit was thus determined as 3.9 ppm.

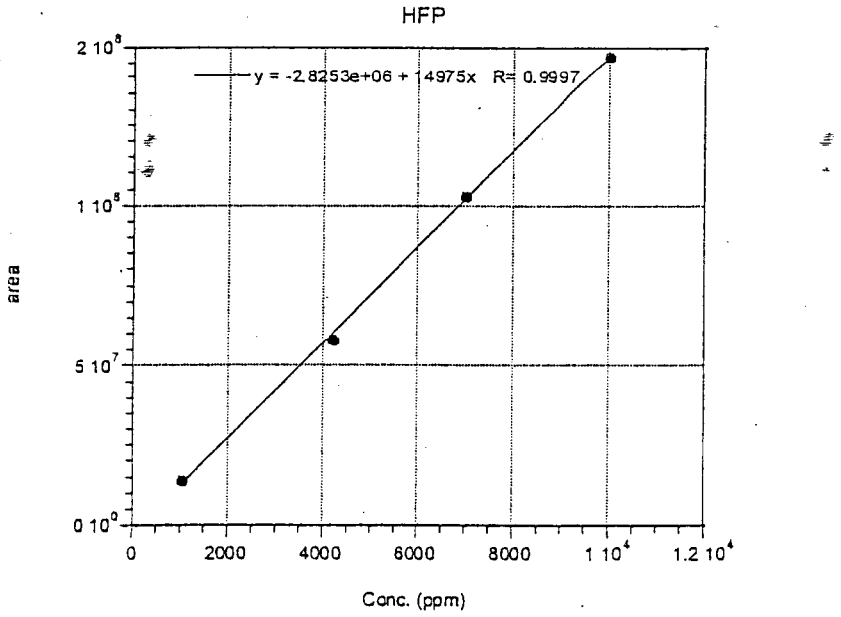

Figure 7. Calibration Plot for HFP

Transport Efficiency

The transport efficiency of each standard was estimated by comparing the measured sample peak area obtained when the sample was injected into injection port in GC1 and passed through combustion reactor and transfer line (system transport) with that obtained when the sample was injected directly into the injection port of GC2 (direct injection).

Table 2. Transport Efficiency

	System Transport			Direct Injection			Efficiency
	Peak Area			Peak Area			(%)
Sample	1st	2nd	AVG (1)	1st	2nd	AVG (2)	(1)/(2)×100
SO_2	9130332	8980717	9055525	11952302	11762267	11857285	76.4
SOF_2	25244352	25203780	25224066	24862639	24773683	24818161	101.6
SO_2F_2	86850304	85572809	86211557	84435720	79738316	82087018	105.0
POSF	1280370	1228718	1254544	1064431	1067947	1066189	117.7
PBSF	159824697	148389773	154107235	25091128	25284200	25187664	611.8
HFP	148679354	145606343	147142849	148372504	142271896	145322200	101.3

The transport efficiencies for SOF_2, SO_2F_2, and HFP were within analytical error. An uncertainty of ± 10 % is reasonable for this type of analysis. That for POSF was slightly higher, but is nonetheless acceptable. That for SO_2 was around 76%. The SO_2 standard was analyzed as a two-component mixture with SOF_2. Since the transport efficiency for SOF_2 was nearly 100%, the results indicate some sample losses for SO_2 through the reactor and transfer lines. Because SO_2 is expected to be one of the major combustion byproducts, we will repeat the efficiency test as part of the Phase III study. We will estimate a SO_2 correction factor based on SO_2 efficiency test results to compensate for its measured concentration during the Phase III study. The efficiency for PBSF was not consistent between the two injection methods. The cause of this discrepancy was discussed with other analytical specialists in our group. The major cause may be a mixing problem of this sample with the solvent, dichloromethane. PBSF is the only liquid phase sample among the six standards. Each time PBSF was diluted with dichloromethane in the GC vials, it was shaken thoroughly in an attempt to obtain a uniform mixture. The density of PBSF is unknown, but expected to be heavier than dichloromethane. This may have caused some settling of the PBSF at the bottom of vials during preparation of the standards. The transport efficiency of PBSF will be re-examined as well as the PBSF calibration if the Phase III combustion tests indicate this is an important combustion intermediate.

Appendix

(Raw Data for Phase II Report)

The total ion chromatograms of the 6 standards (SO_2, SOF_2, SO_2F_2, POSF, PBSF, and hexafluoropropene (HFP)) and the mass spectra corresponding to standard peaks are presented below. Mass spectra are shown for the highest, detection limit, and below detection limit concentrations for each standard.

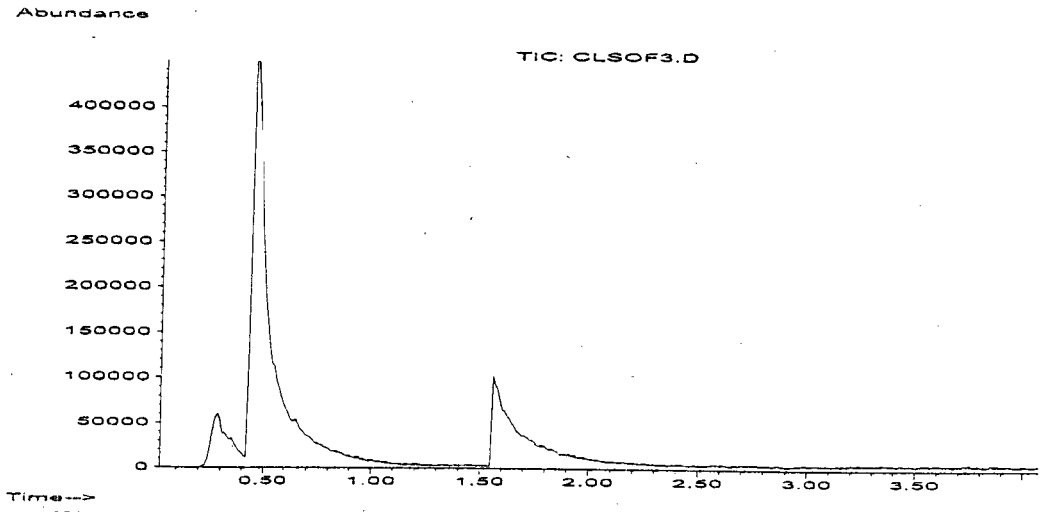

Figure 8. Total Ion Chromatogram for SOF_2 (3034 ppm) and SO_2 (1570 ppm)

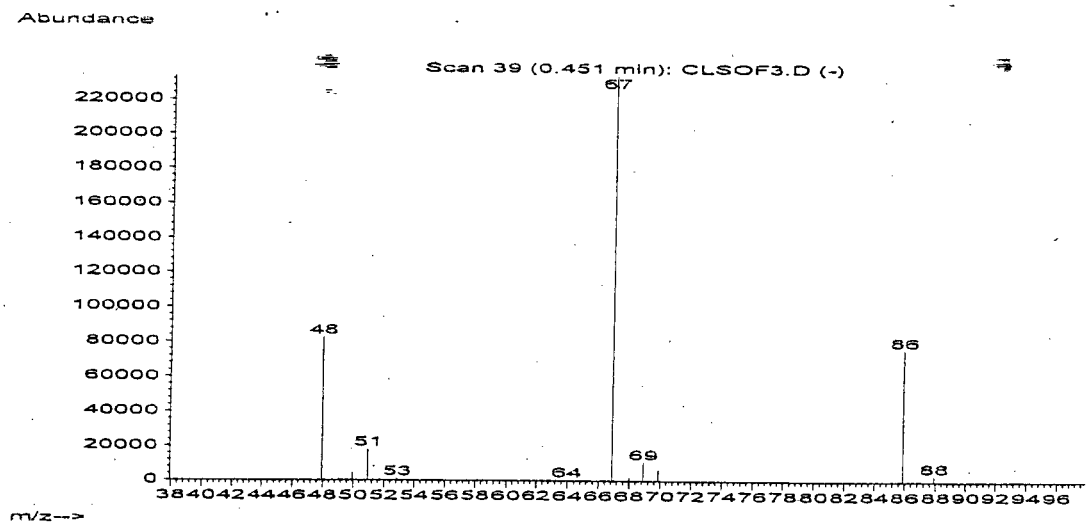

Figure 9. Mass Spectra for SOF_2 (3034 ppm)

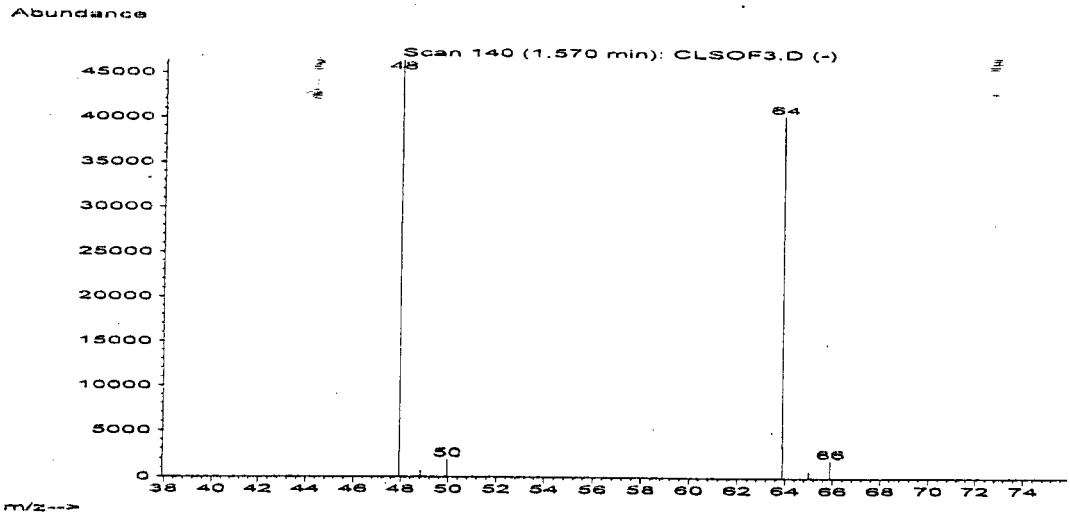

Figure 10. Mass Spectra for SO_2 (1570 ppm)

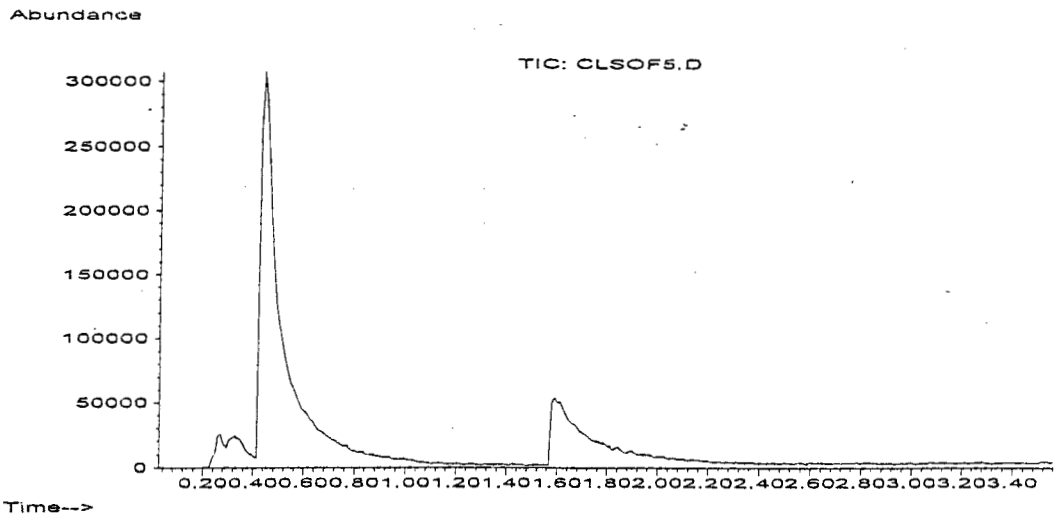

Figure 11. Total Ion Chromatogram for SOF_2 (2124 ppm) and SO_2 (1099 ppm)

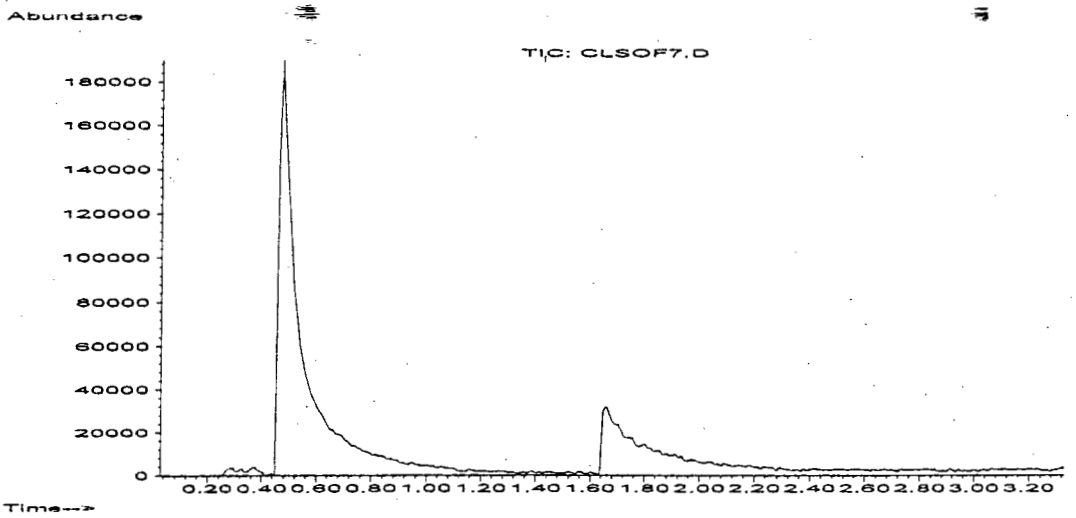

Figure 12. Total Ion Chromatogram for SOF_2 (1214 ppm) and SO_2 (628 ppm)

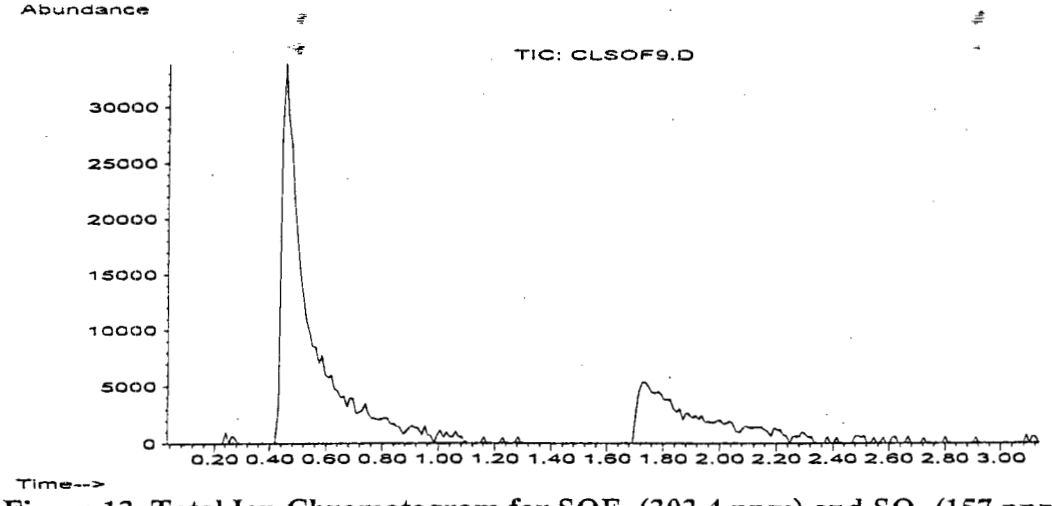

Figure 13. Total Ion Chromatogram for SOF_2 (303.4 ppm) and SO_2 (157 ppm)

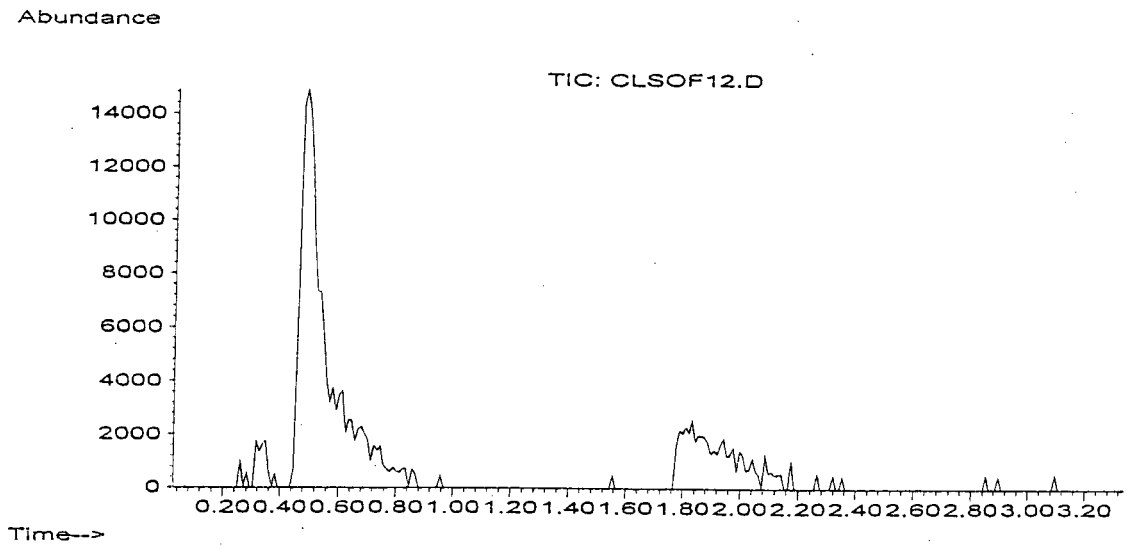

Figure 14. Total Ion Chromatogram for SOF_2 (151.7 ppm) and SO_2 (78.5 ppm)

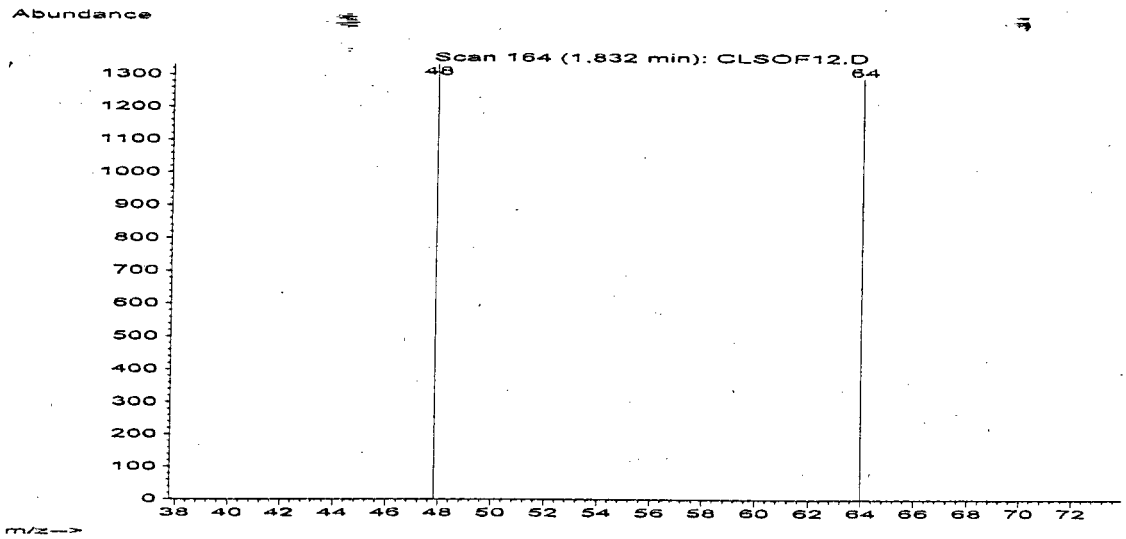

Figure 15. Mass Spectra for SO_2 (78.5 ppm)

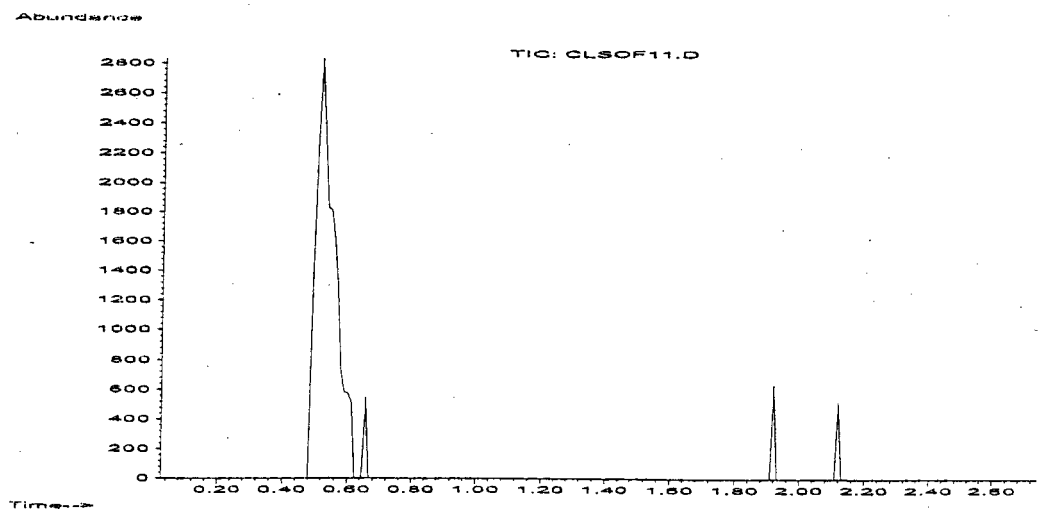

Figure 16. Total Ion Chromatogram for SOF_2 (30.3 ppm) and SO_2 (15.7 ppm)

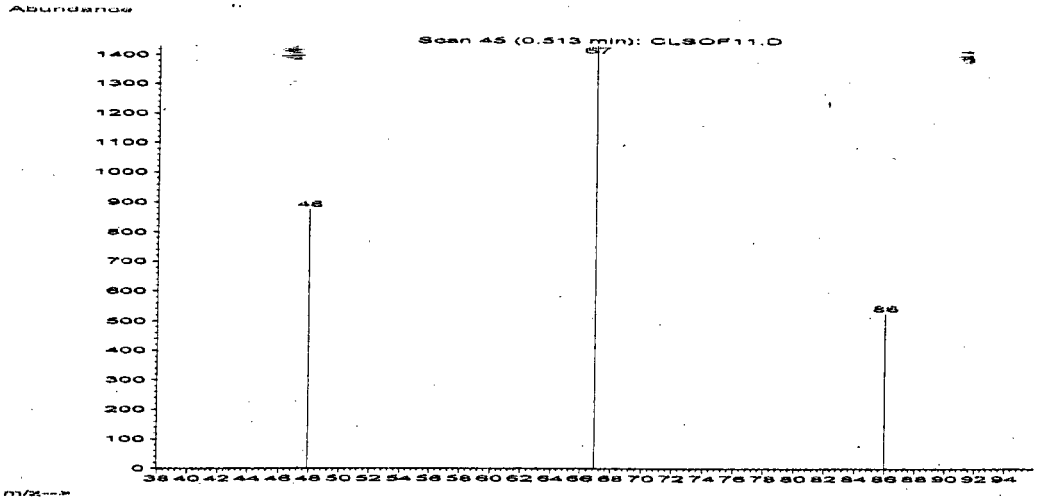

Figure 17. Mass Spectra for SOF_2 (30.3 ppm)

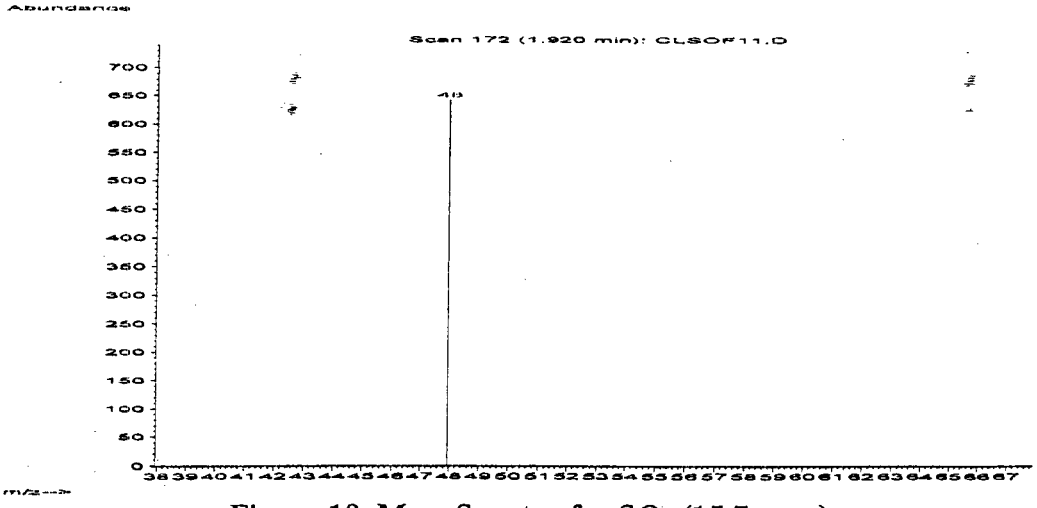

Figure 18. Mass Spectra for SO_2 (15.7 ppm)

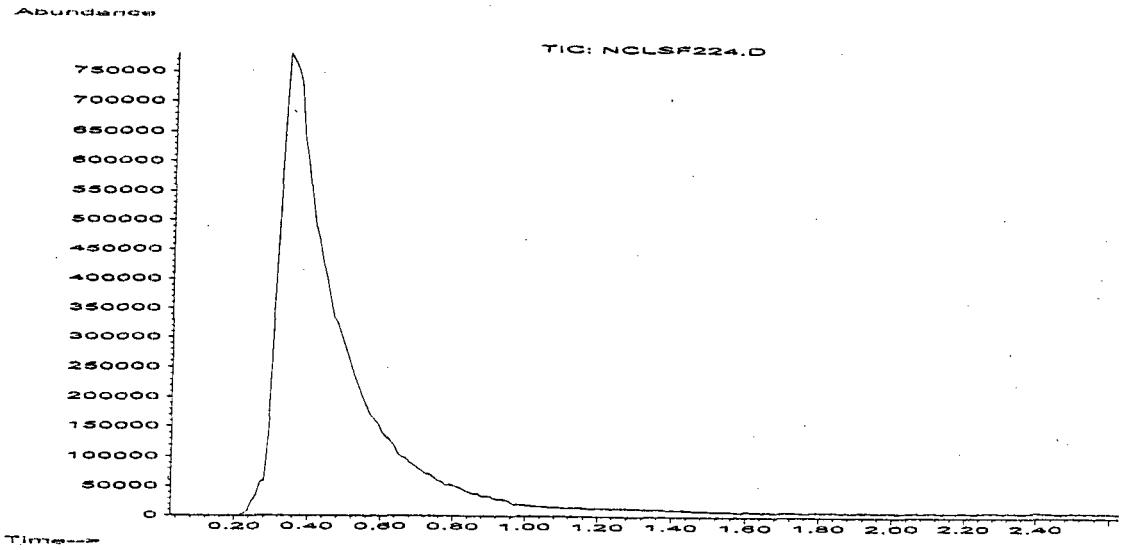

Figure 19. Total Ion Chromatogram for SO_2F_2 (10049 ppm)

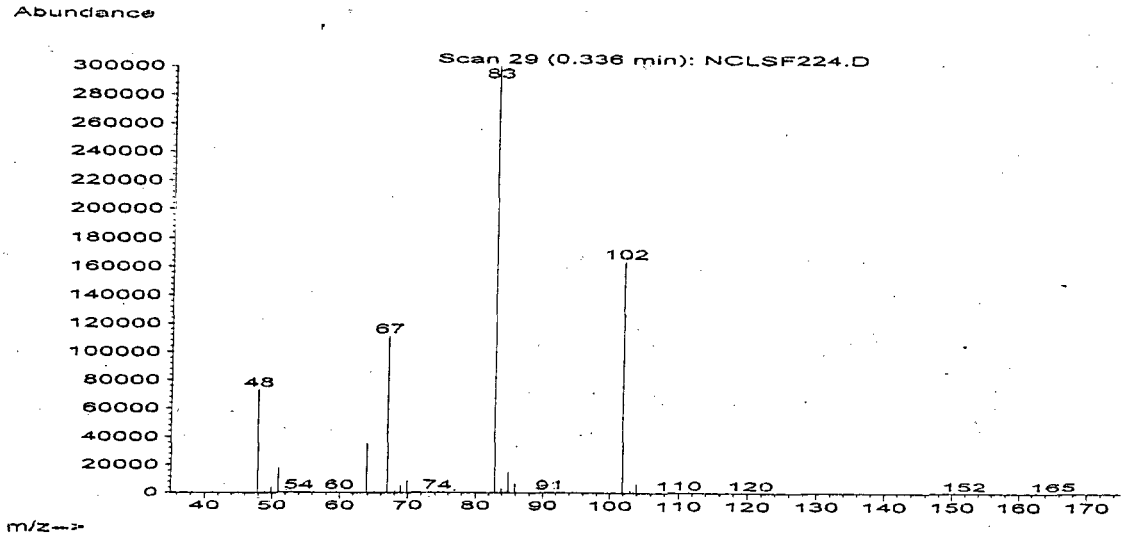

Figure 20. Mass Spectra for SO_2F_2 (10049 ppm)

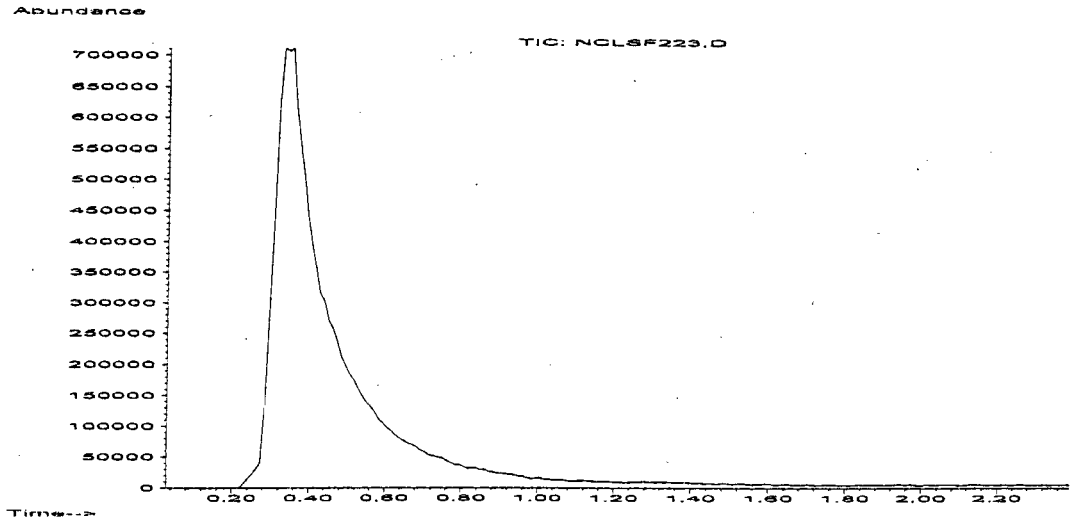

Figure 21. Total Ion Chromatogram for SO_2F_2 (7034 ppm)

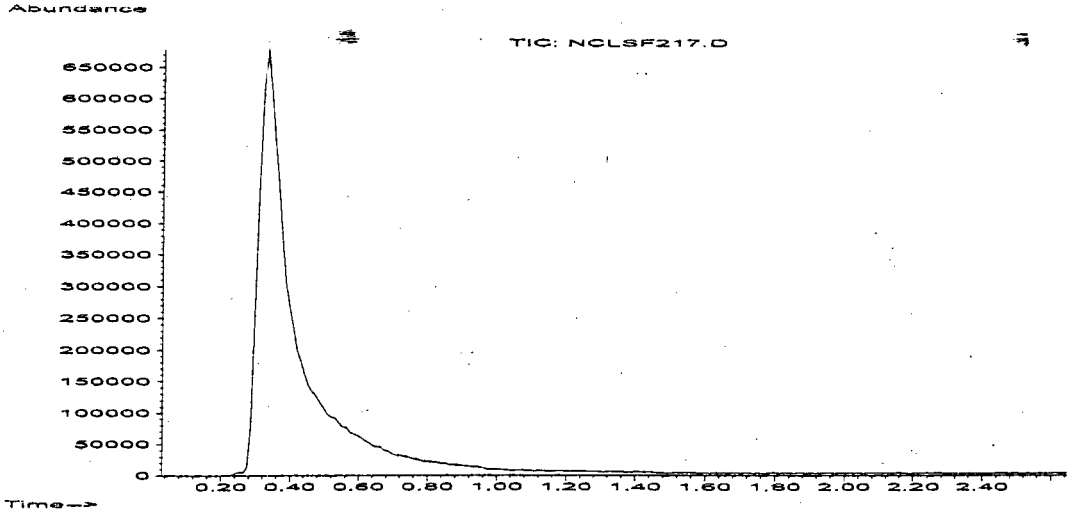

Figure 22. Total Ion Chromatogram for SO_2F_2 (4020 ppm)

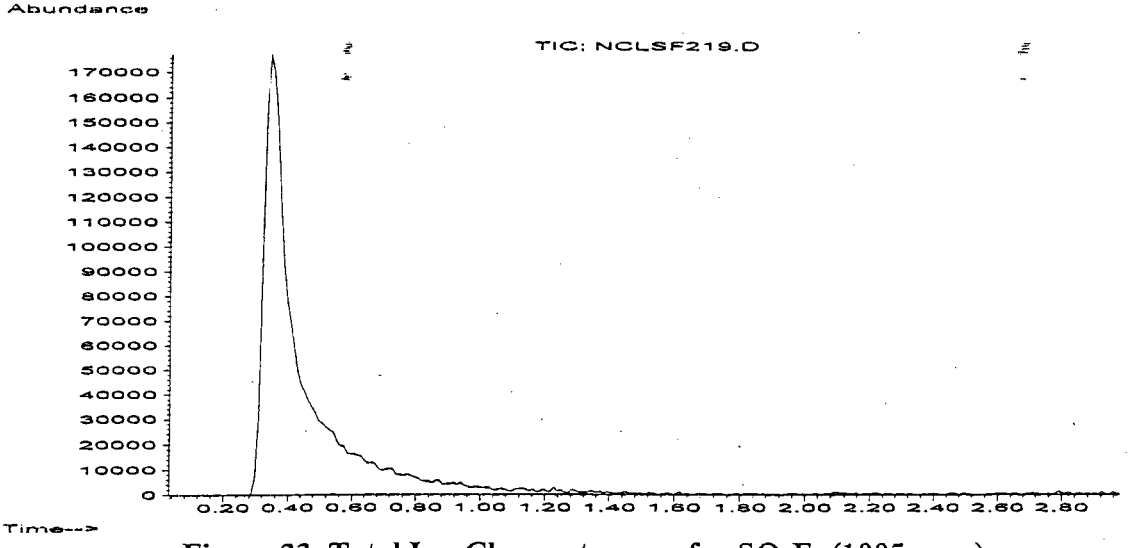

Figure 23. Total Ion Chromatogram for SO_2F_2 (1005 ppm)

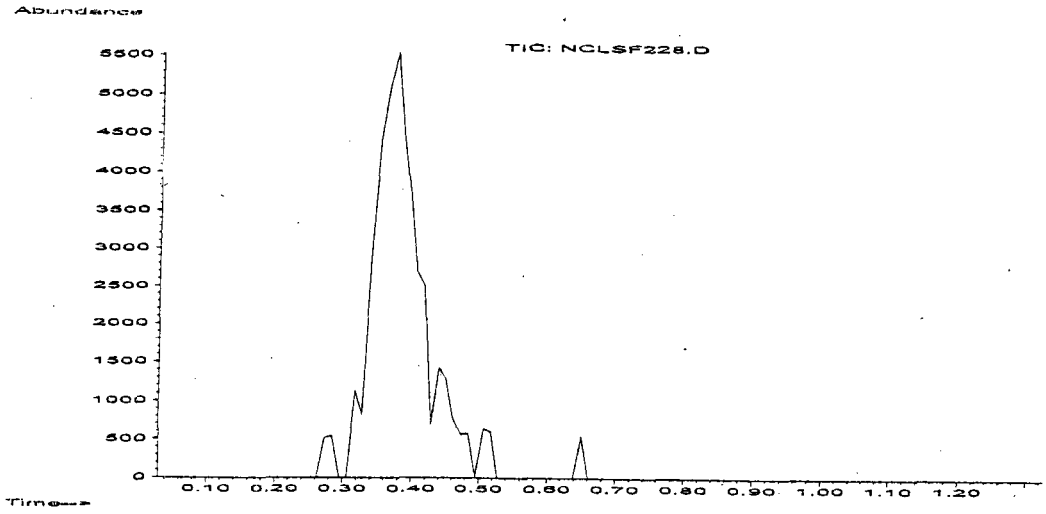

Figure 24. Total Ion Chromatogram for SO_2F_2 (20.1 ppm)

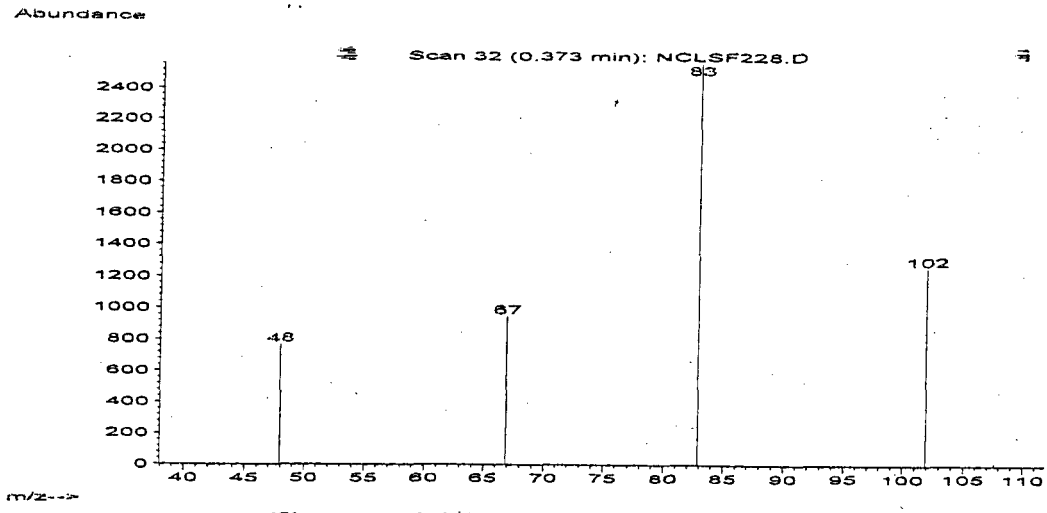

Figure 25. Mass Spectra for SO_2F_2 (20.1 ppm)

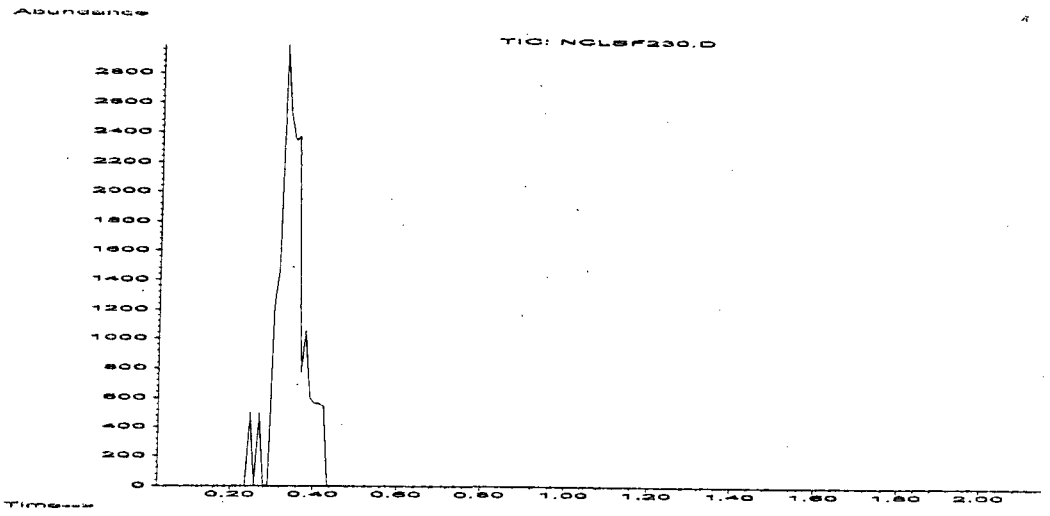

Figure 26. Total Ion Chromatogram for SO_2F_2 (4.0 ppm)

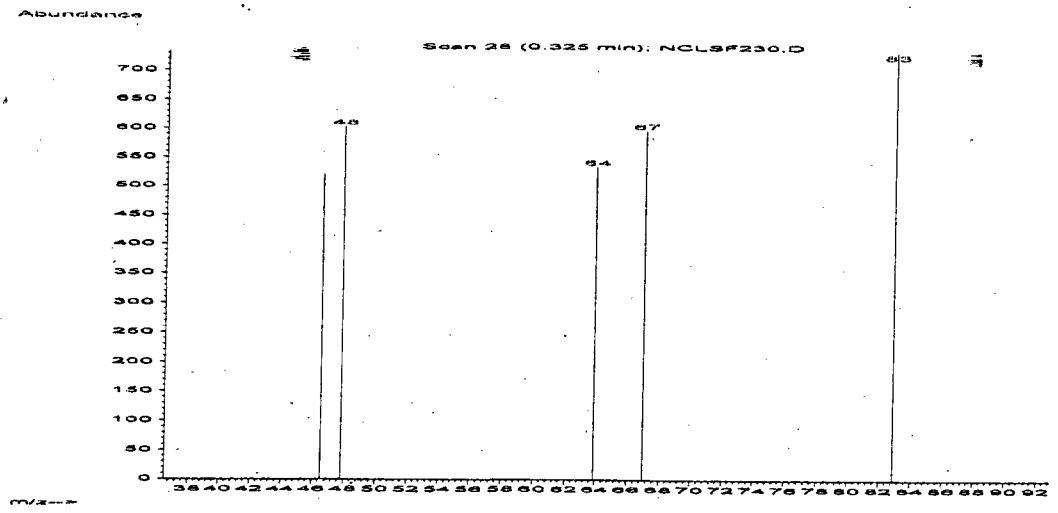

Figure 27. Mass Spectra for SO_2F_2 (4.0 ppm)

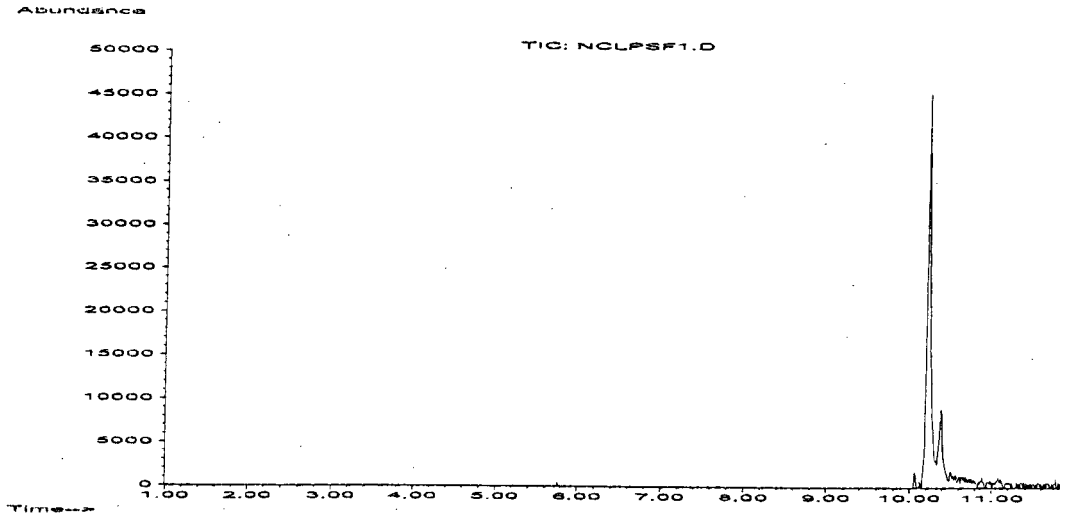

Figure 28. Total Ion Chromatogram for POSF (20.1 ppm)

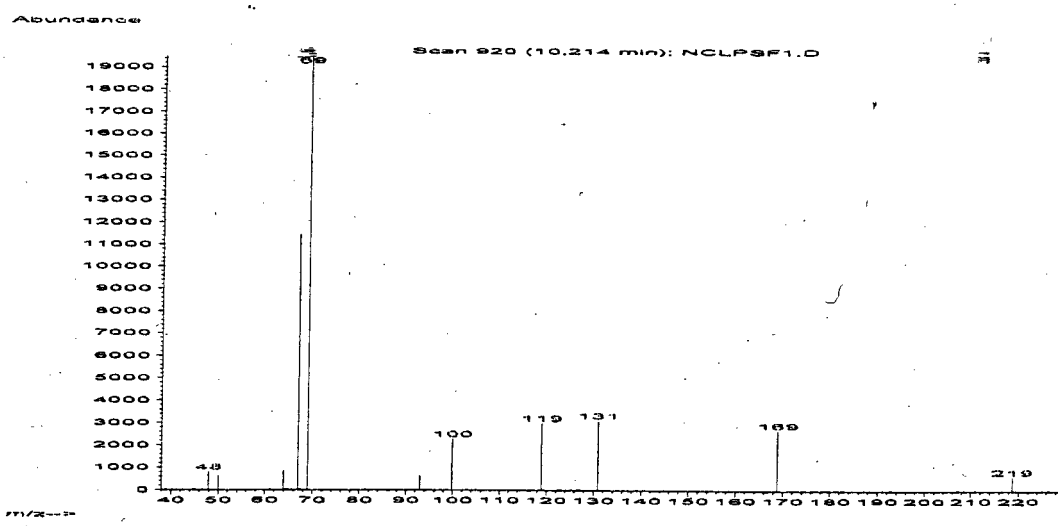

Figure 29. Mass Spectra for POSF (20.1 ppm)

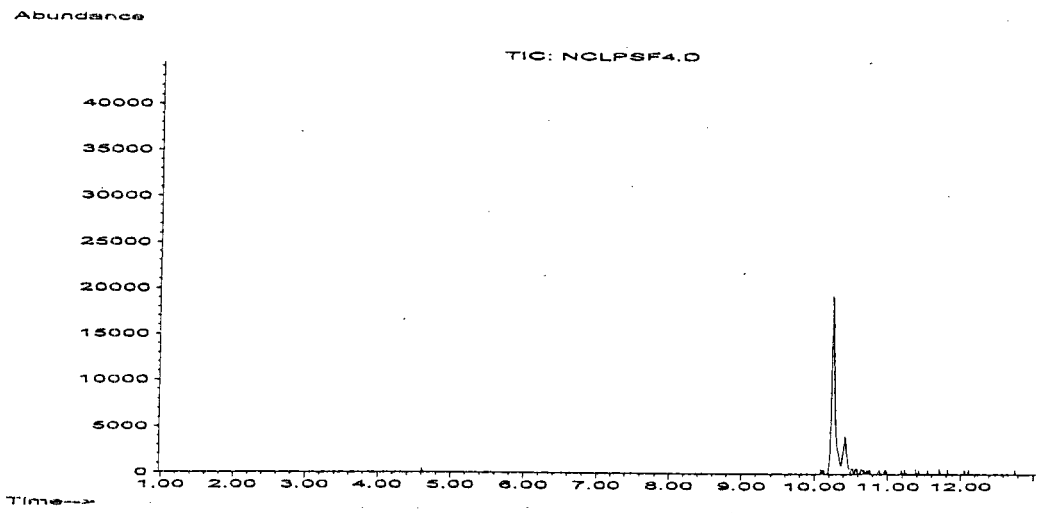

Figure 30. Total Ion Chromatogram for POSF (14.1 ppm)

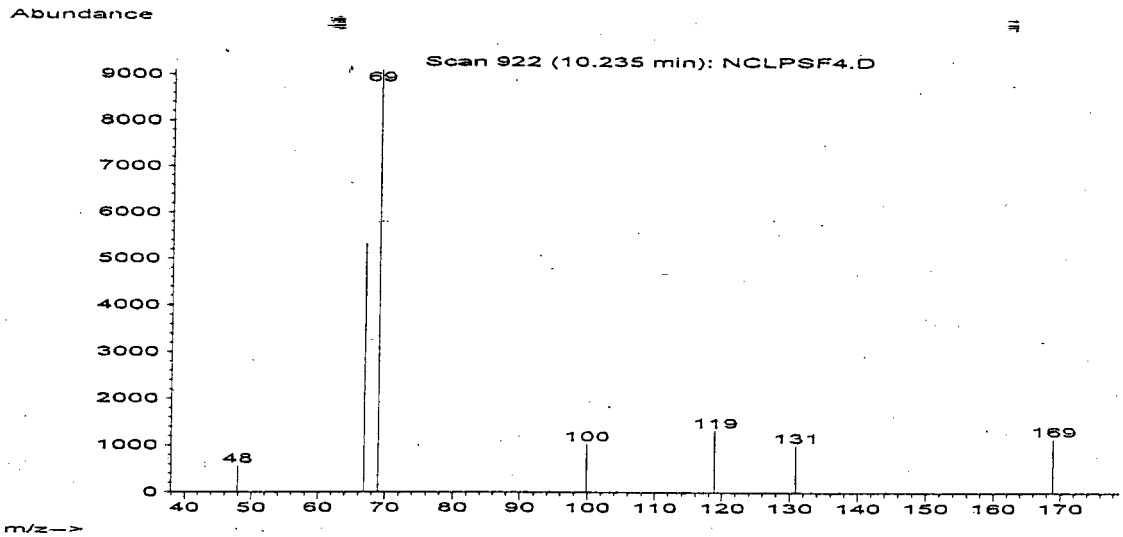

Figure 31. Mass Spectra for POSF (14.1 ppm)

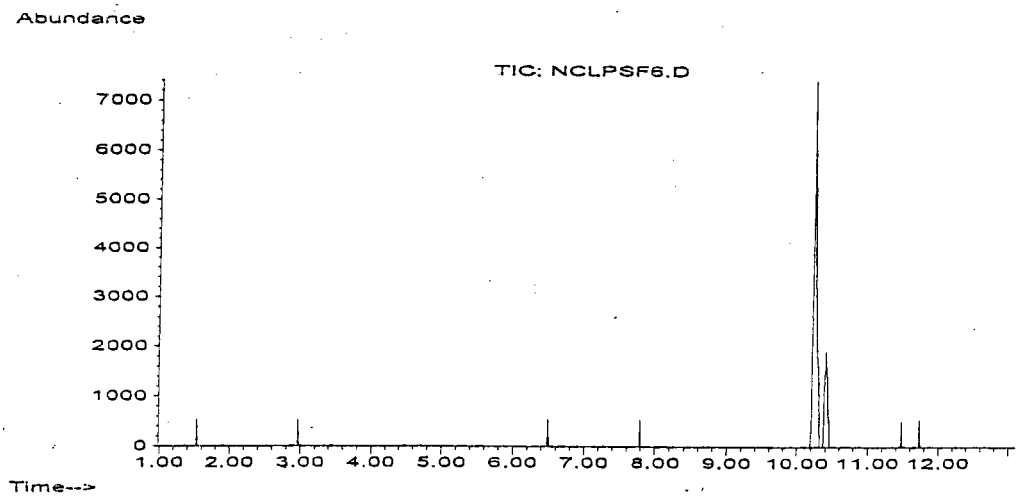

Figure 32. Total Ion Chromatogram for POSF (8.0 ppm)

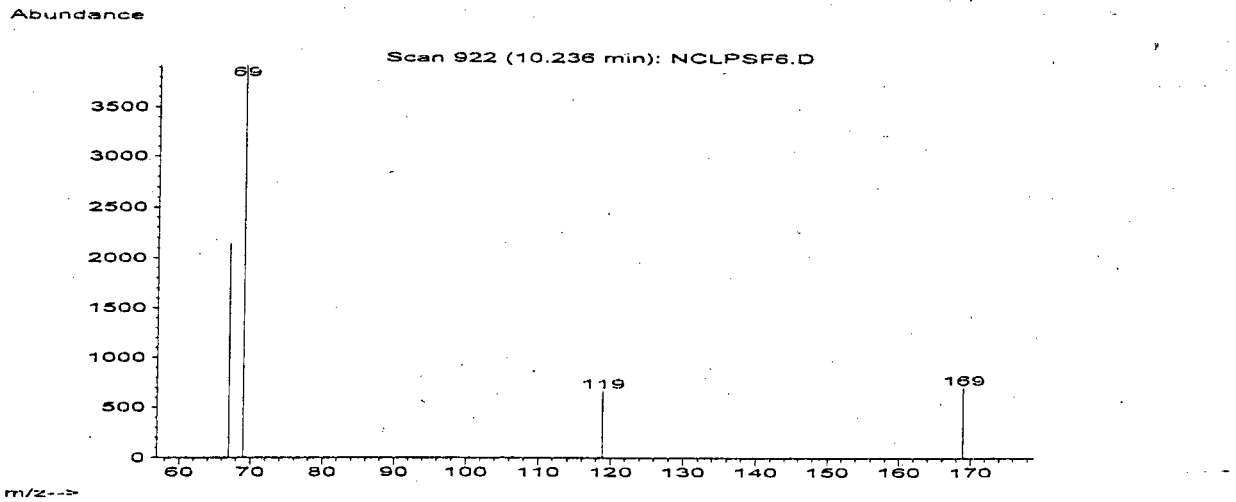

Figure 33. Mass Spectra for POSF (8.0 ppm)

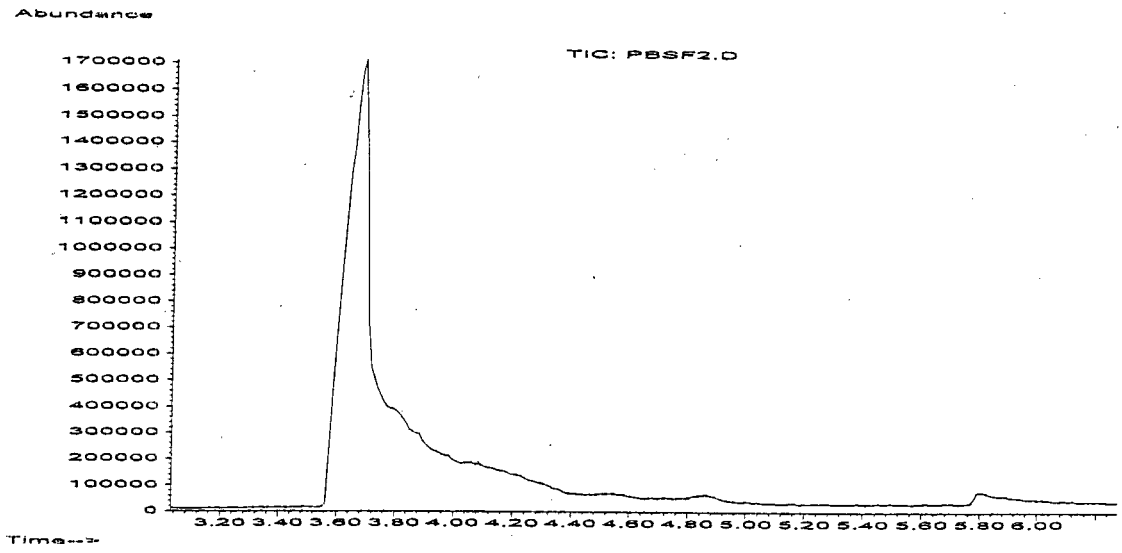

Figure 34. Total Ion Chromatogram for PBSF (1000 ppm)

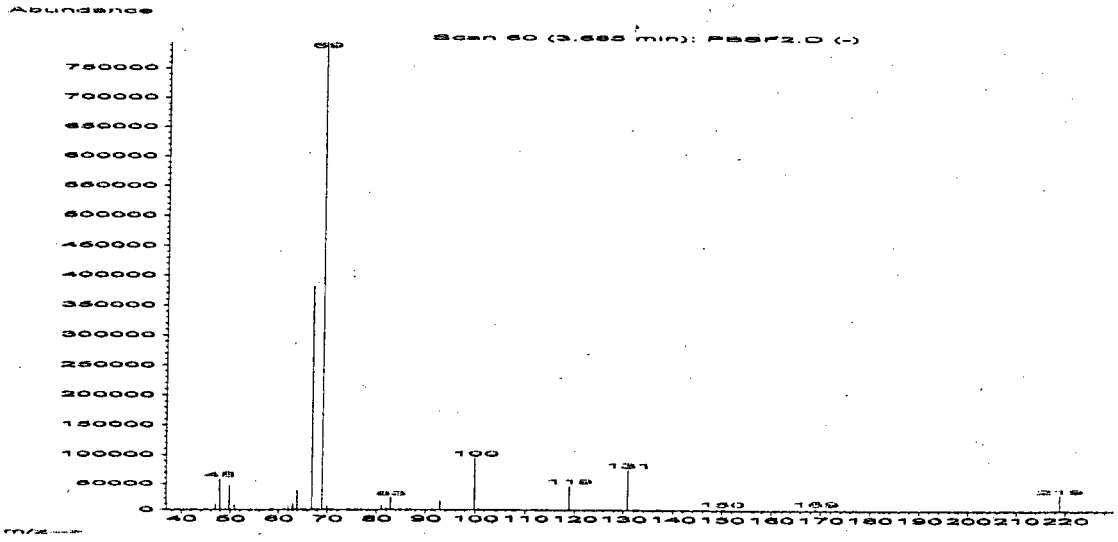

Figure 35. Mass Spectra for PBSF (1000 ppm)

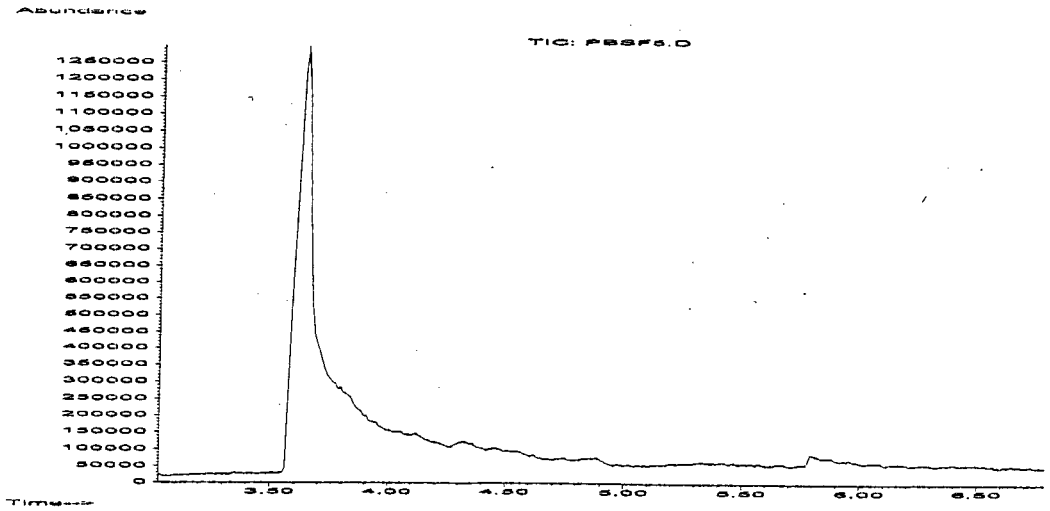

Figure 36. Total Ion Chromatogram for PBSF (700 ppm)

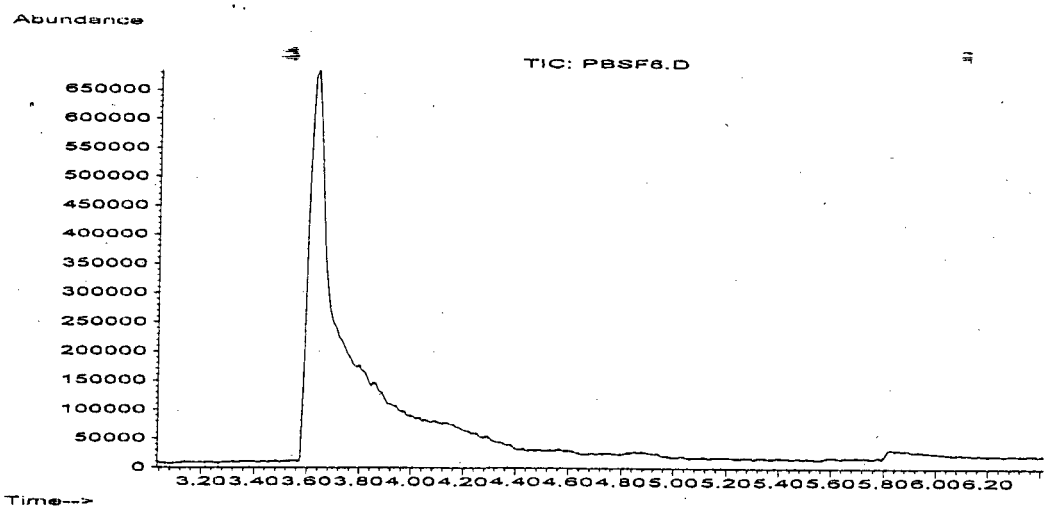

Figure 37. Total Ion Chromatogram for PBSF (400 ppm)

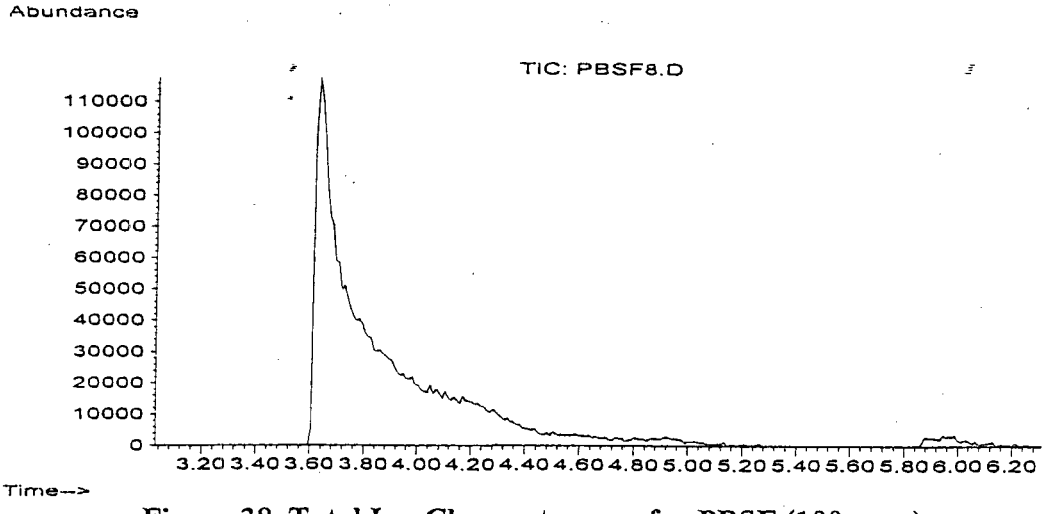

Figure 38. Total Ion Chromatogram for PBSF (100 ppm)

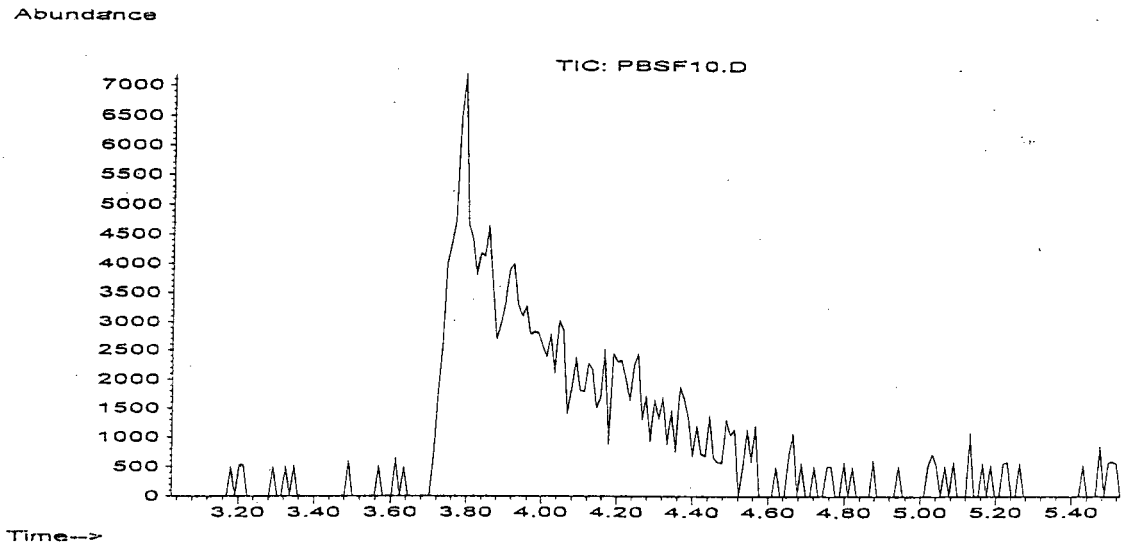

Figure 39. Total Ion Chromatogram for PBSF (10 ppm)

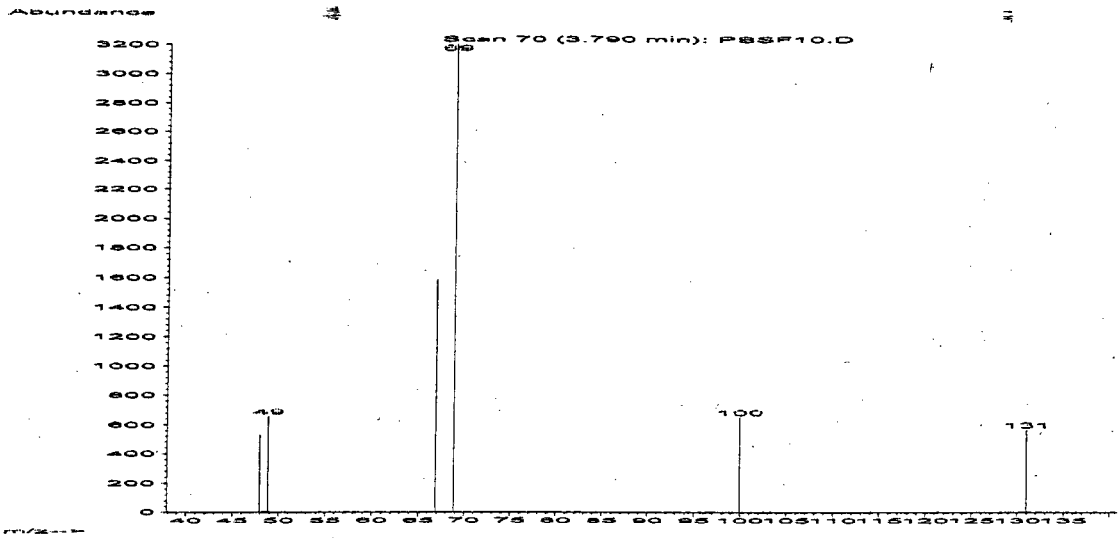

Figure 40. Mass Spectra for PBSF (10 ppm)

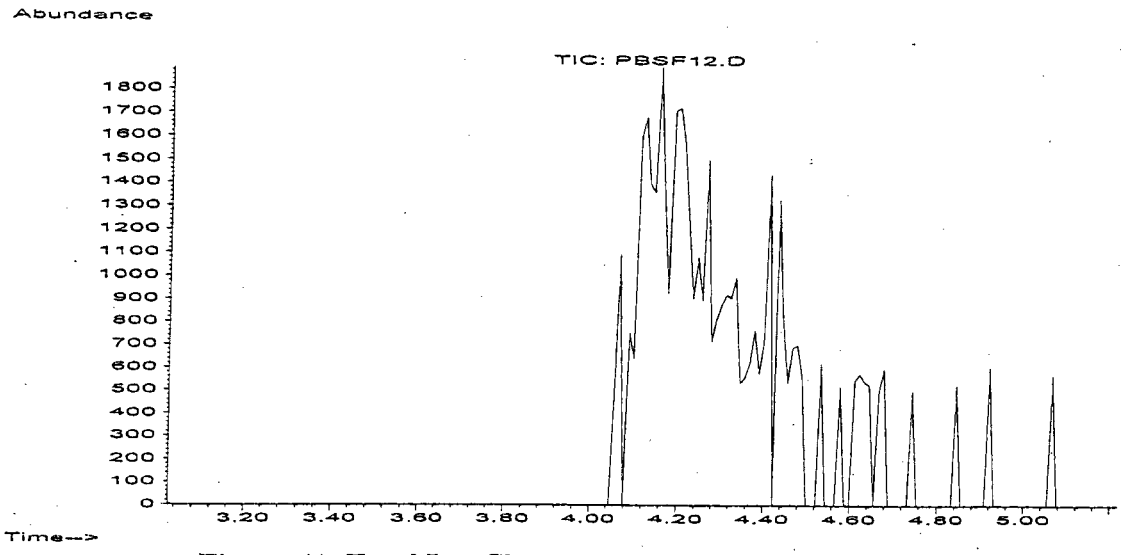

Figure 41. Total Ion Chromatogram for PBSF (5 ppm)

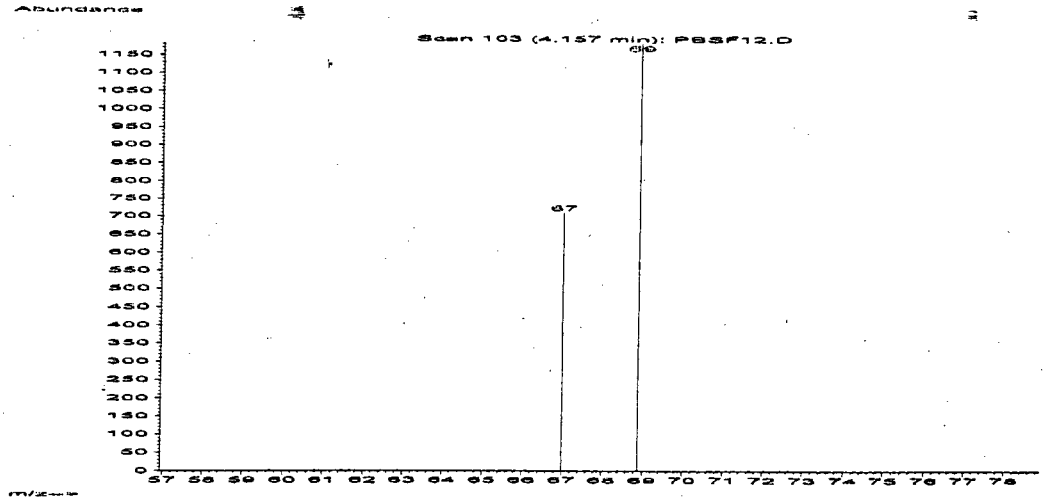

Figure 42. Mass Spectra for PBSF (5 ppm)

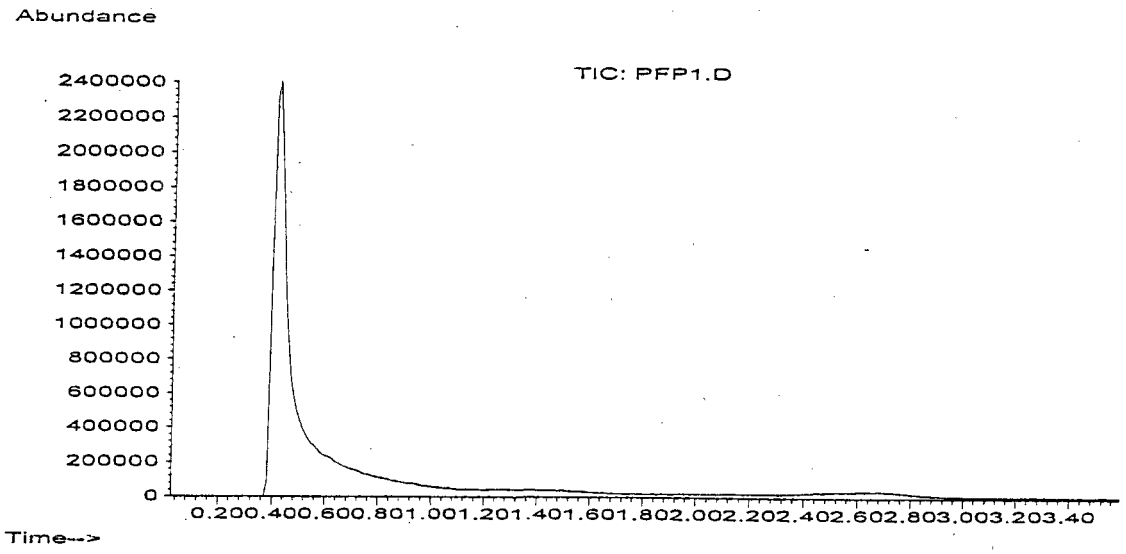

Figure 43. Total Ion Chromatogram for Hexafluoropropene (HFP) (10,000 ppm)

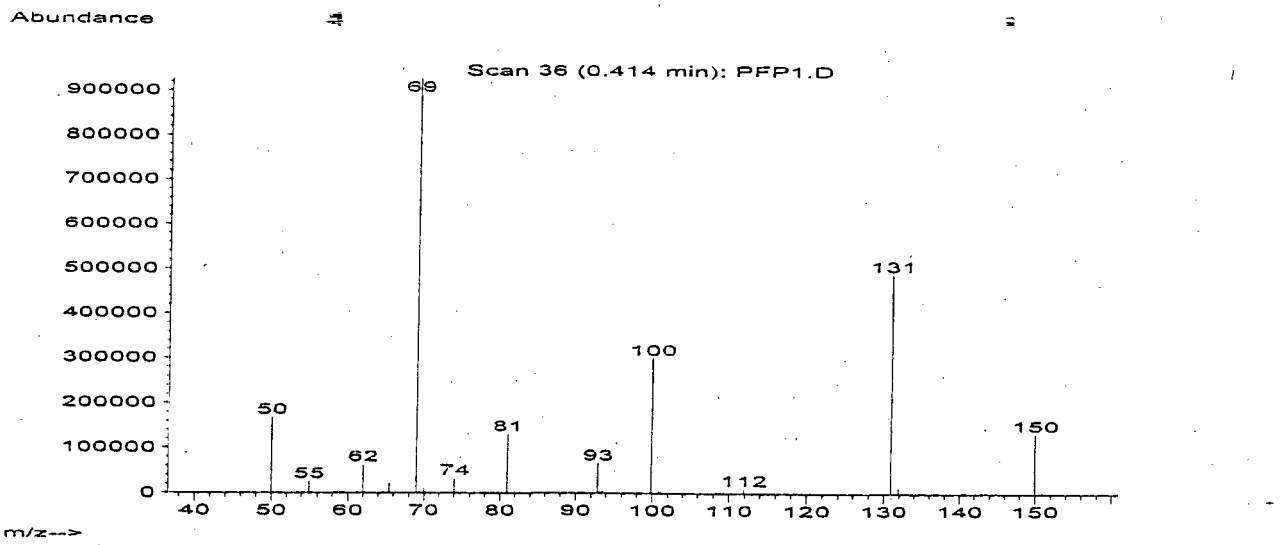

Figure 44. Mass Spectra for HFP (10,000 ppm)

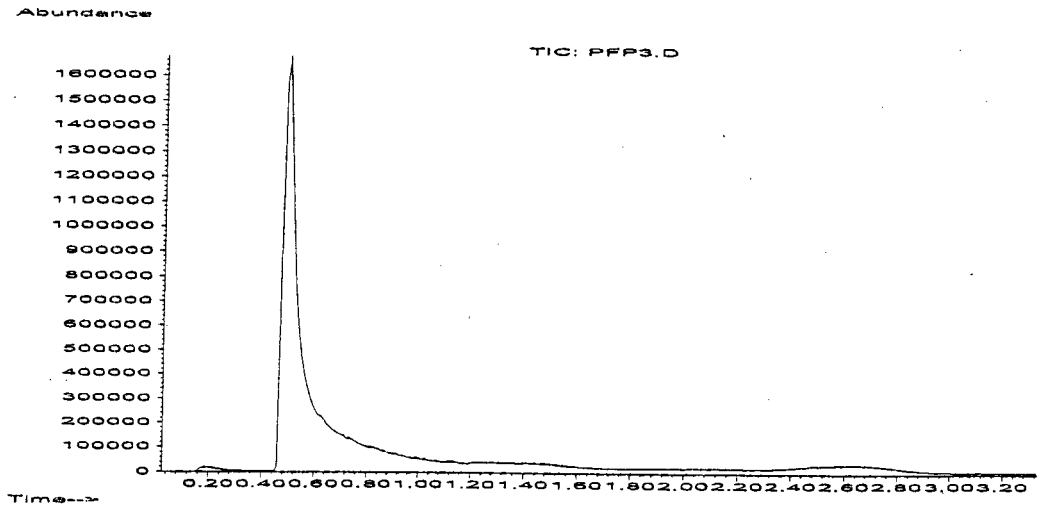

Figure 45. Total Ion Chromatogram for HFP (7,000 ppm)

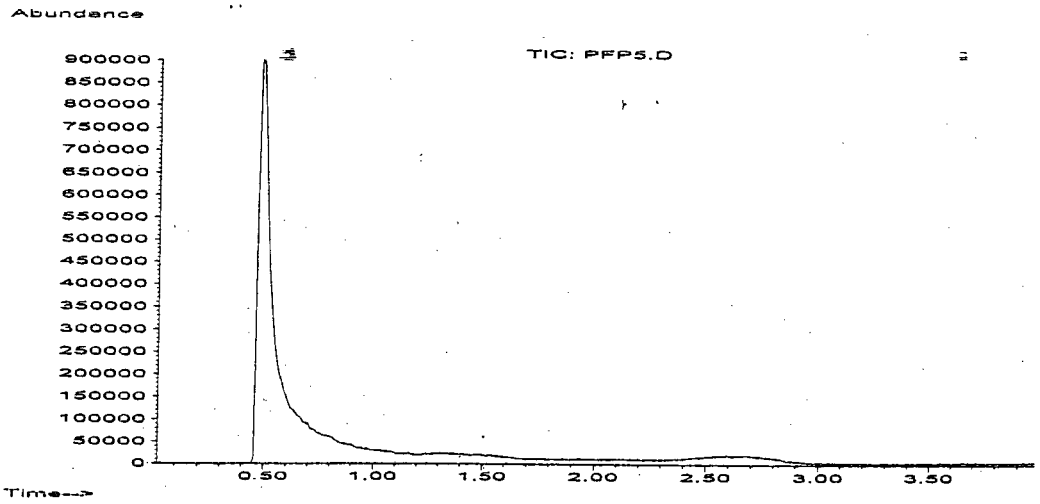

Figure 46. Total Ion Chromatogram for HFP (4,200 ppm)

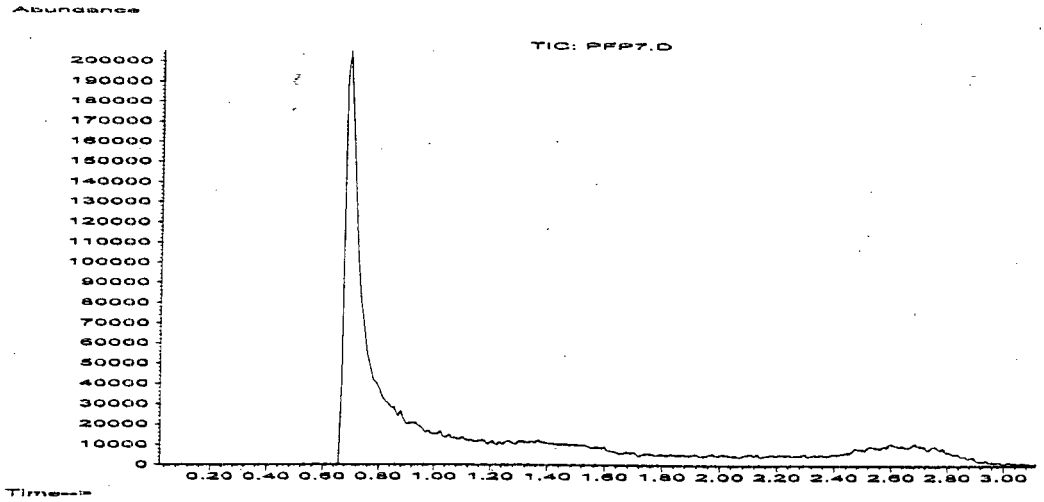

Figure 47. Total Ion Chromatogram for HFP (1,050 ppm)

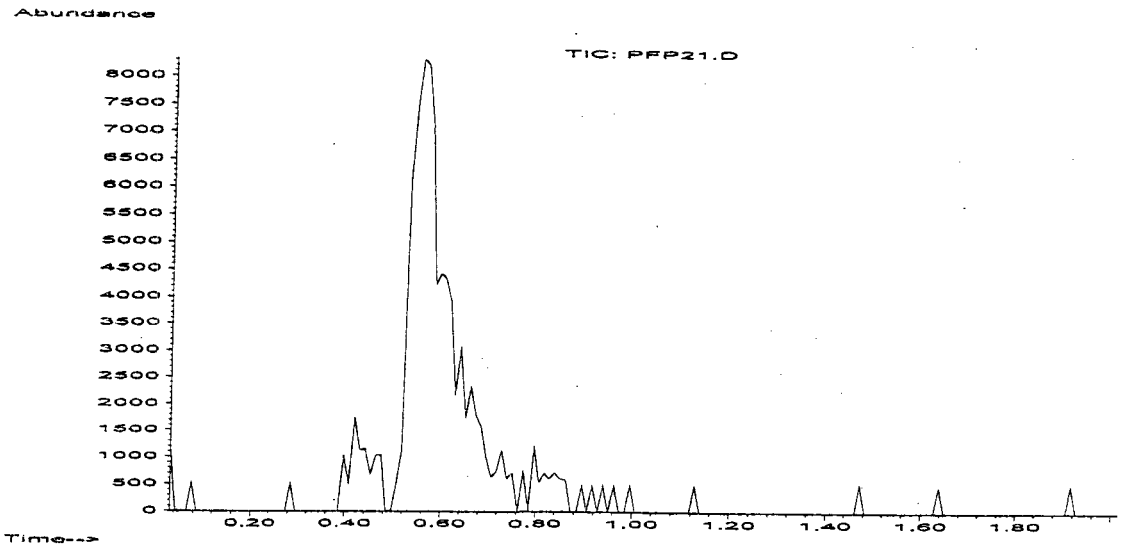

Figure 48. Total Ion Chromatogram for HFP (3.9 ppm)

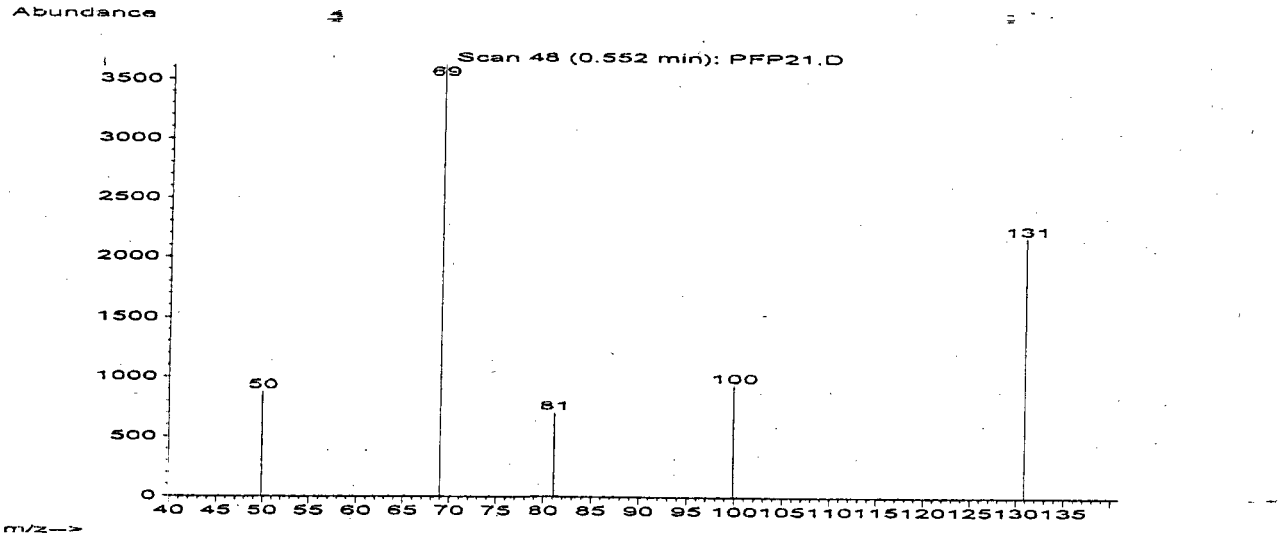

Figure 49. Mass Spectra for HFP (3.9 ppm)

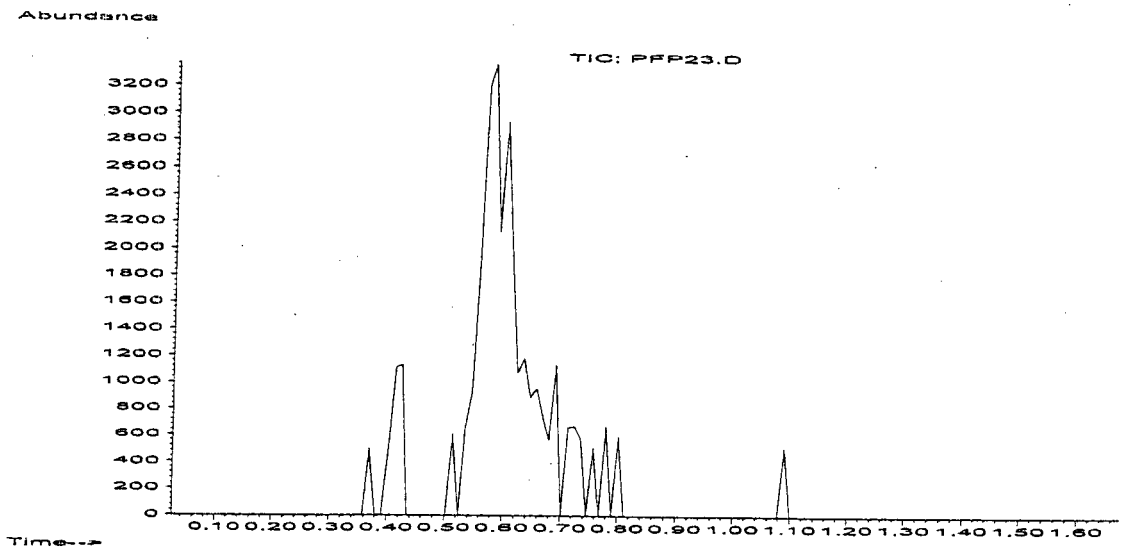

Figure 50. Total Ion Chromatogram for HFP (1.9 ppm)

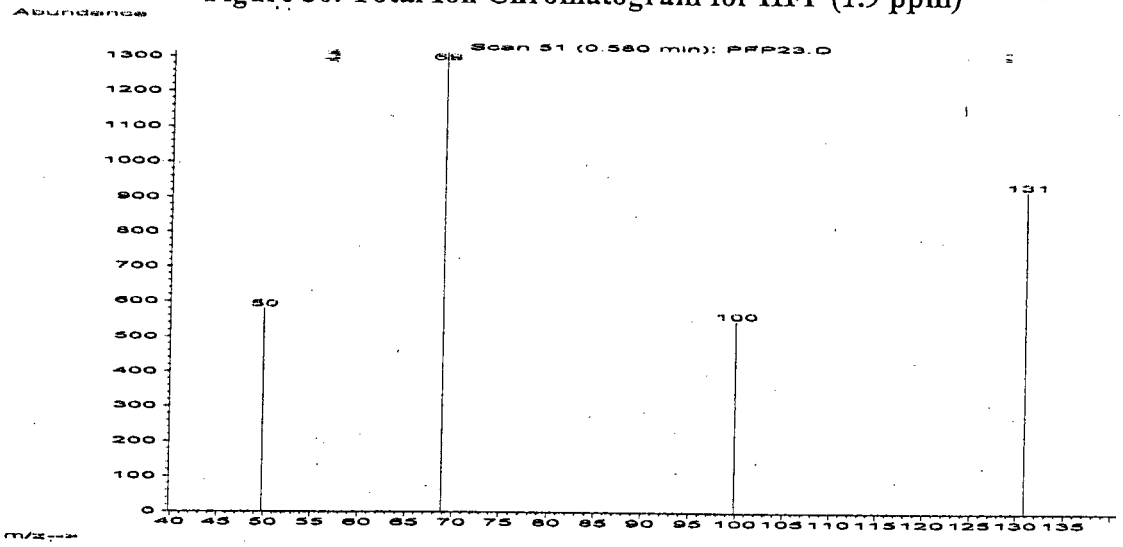

Figure 51. Mass Spectra for HFP (1.9 ppm)

Appendix 3

Phase III Test Protocol and Addendum

July 30, 2002

Phase III Protocol: Laboratory-Scale Thermal Degradation of Perfluoroalkyl Sulfonates and Perfluoroalkyl Sulfonamides

Prepared by:
Environmental Sciences and Engineering Group
University of Dayton Research Institute

Summary

The phase III study will consist of 6 separate tests as shown in Figure 1. The main objective of this study is the simulation of the incineration of seven fluorocarbon-based samples provided by 3M. Specific attention is being given to the potential formation of PFOS and PFBS during the incineration of these materials. In-line and off-line GC/MS analysis, PUF (polyurethane foam) sample collection and condensed phase sample extraction will be conducted. In the latter two tests, the PUF cartridges and the extracts will be delivered to 3M for analysis of PFOS and PFBS by LC/MS. Prior to the sample combustion analysis, the transfer efficiency for SO_2 will be reexamined and the laboratory spike analysis for PFOS and PFBS will be performed. A heated blank line analysis will be performed at the onset of the sample combustion tests. After the combustion tests, another heated blank line analysis will be performed. Transfer efficiency tests for $C_4F_9SO_3^-K^+$, and $C_8F_{17}SO_3^-K^+$ will be performed at the conclusion of the phase III study.

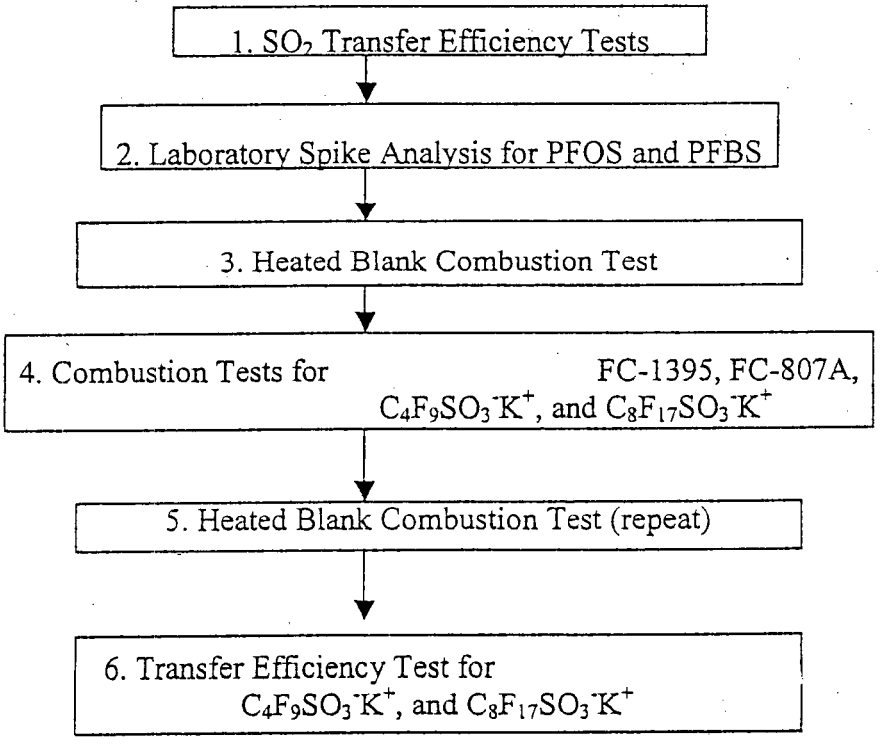

Figure 1. Chronological summary of tests to be conducted during Phase III.

1. SO_2 Transfer Efficiency Tests

In the phase II transfer efficiency test, sulfur dioxide (SO_2) showed recovery efficiency of 76.4 %. The SO_2 standard was analyzed as a two-component mixture with SOF_2 (thionyl fluoride) and the SOF_2 recovery rate was nearly 100%. Therefore, it is quite conceivable that SO_2 was absorbed on the surface of reactor and transfer line. We will conduct another analysis to confirm this result and to estimate the recovery coefficient for the calculation of SO_2 concentration from the combustion tests.

2. Laboratory Spike Analysis for PFOS and PFBS

A 1 μg sample will be used for the PFOS and PFBS spike analysis. This is the amount of PFOS or PFBS that would be formed if 0.1% of the perfluoroalkyl portion of the fluorochemical products used in this study were converted to one of these compounds in the reactor. Analysis of the extracts from these spiked reactor/transport systems will show if this amount of PFOS or PFBS can be extracted and detected accurately. 10 mg of PFOS and PFBS will be dissolved with 10 ml methanol (Aldrich, HPLC grade) and 1 μl of solution (containing 1μg of PFOS and PFBS) will be placed into a reactor (4 mm (i.d.) × 6 mm (o.d.) × 7 cm length) and dried by blowing high purity nitrogen, or bottled dry air over it at a rate that won't blow droplets out the other end. After the drying process, the transfer line will be assembled and extraction will be performed using the same lot of methanol used to dissolve the samples. The total volume of entire reactor and transfer line is 1.1 ml as shown in detail below.

Total volume of transfer line	= 0.2 ml: as measured
Reactor volume	= 0.9 ml: as calculated (0.2 cm × 0.2 cm × 3.14 × 7 cm)
Total	= 1.1 ml

The concentration of PFOS and PFBS in the spike that is extracted with five times volume of reactor/transfer line (using methanol as the solvent) will be 180 ng/ml. This is 18 times 3M's estimated detection limit for PFOS and PFBS (ca. 10 ng/ml).

Figure 2 shows a schematic of the PFOS and PFBS laboratory control spike extraction system. The extraction procedure will be based on the perspective that only the condensation of PFOS/PFBS subsequent to the high-temperature combustion stage would be indicative of likely PFOS/PFBS release to the environment from actual incineration systems. Thus, the extraction procedure will focus on the high-temperature reactor (downstream of the highest temperature point) and the reaction product transfer lines between the reactor and the various sample collection systems. The following paragraph describes the analytical extraction procedure.

The end of a 1/16" tee will be capped prior to extraction. The total amount of methanol used will be 5.5 ml, five times the volume of the reactor/transfer line. The methanol will be stored in 40 ml vials (Wheaton CLEAN-PAK, clear certified with pre-cleaned lined cap) and the vials will be connected to the end of 1/16" tubing using 1/16" stainless tubing. The other end of reactor will be connected to another 40 ml vial (Wheaton CLEAN-PAK, clear certified with pre-cleaned lined cap) using 1/8" stainless tubing. Methanol will be slowly injected into the system by pressurizing a methanol reservoir by helium gas flow (2.7ml/min) until all methanol is injected

into the system. The initial methanol (5.5 ml) level will be marked on the 40 ml vial prior to collection and will be used for confirming that all of sample introduced is collected. The extraction will be performed twice for each sample. The collected samples will be secured, labeled, and appropriately packaged for overnight delivery to 3M Environmental Laboratory with one blank vial (40 ml) containing 5.5 ml methanol.

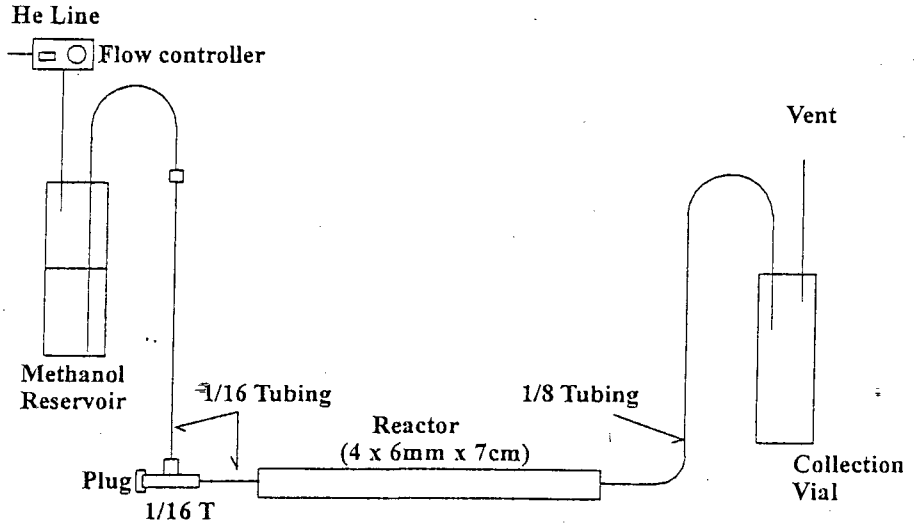

Figure 2. Experimental set up for PFOS and PFBS laboratory control spike tests.

3. Heated Blank Combustion Analysis

Before and after the sample combustion tests, a heated blank combustion test will be conducted for a reactor temperature at 600 and 900°C to examine system contamination. The sample collection will be performed twice for each temperature (one for the sample collection using polyurethane foam (PUF, (Supelco ORBO PUF Cartridge)) and one for the sample collection using Tedlar sampling bags (0.5L, SKC Inc.). Two GC-MS analyses with different GC columns will be conducted for the heated blank exhaust gas analysis (one with in-line GC-MS analysis and one with off-line GC-MS analysis). After the gas-phase collection and analysis, the reactor will be cut in half and condensed phase product extraction will be performed using the method previously outlined in Section 2.

Figure 3 shows the schematic diagram of the experimental setup to conduct in-line GC/MS analysis and PUF sample collection for the heated blank combustion test. It also shows the detailed dimensions of the reactor/transfer line system. For off-line GC/MS analysis, the PUF shown in Figure 3 will be replaced by a Tedlar bag. Compressed air will be delivered both to the pyroprobe chamber and the reactor. The total air flow rate will be 10.3 and 7.6 ml/min (with 0.8 and 0.7 ml/min to the pyroprobe chamber) for reactor temperatures of 600 and 900°C, respectively. The residence time in the reactor (4 mm i.d. × 6 mm o.d. × 14 cm length with 8 cm effective length) will be ca. 2.0 s. The determination of the effective length of the reactor is discussed in Section 4. The flow rate will be controlled within ±10 % error. A majority of the

effluent will pass through the PUF cartridge for sample collection and 1 ml/min will be directed into the GC column for in-line analysis.

In-line GC-MS Analysis: A HP5890A/5970B series GC-MS with DB-5 MS capillary column (30 m length, 0.25 mm i.d., Agilent Technologies, Inc.) will be used for the phase III study. The initial temperature of GC2 will be held at -60°C and sample will be concentrated at the head of the column for 2 and 2.5 (±5%) min for reactor temperature of 600 and 900°C, respectively. During this time period, PUF combustion effluent sample collection will also take place. Two PUF cartridges will be placed in series as shown in Figure 3. After the sample collection, switching valve 1 will be turned to (1) position in Figure 3 to pressurize the GC column. As soon as pressurization begins, the temperature programming of GC2 will be started. The initial temperature will be held for 1 minute and the temperature will be raised at 10°C/min up to 260°C. The final temperature will be held for 5 minutes. Also after the switching valve 1 is turned to (1) position for the GC column pressurization, the PUF cartridges will be removed from the system. The PUF cartridges will be secured, labeled, and appropriately packaged for next business day delivery to 3M Environmental Laboratory with one blank PUF.

Off-line GC-MS Analysis: After the PUF sampling collection, identical sample collection will be performed using a Tedlar sampling bag. The collected off gas will be sampled within 15 min. of collection and analyzed using HP5890A/5970B series GC-MS with SPEL-Q PLOT (Porous Layer Open Tubular) column (30 m length, 0.53 mm i.d., SUPELCO). The Tedlar bags will be heated to ca. 50 – 60°C to ensure that all of the sulfur compounds that are soluble in the condensed water vapor present in the bag are partitioned into the gas-phase. This column will capture the light compounds ($<C_6$) that the DB-5 MS capillary column may not effectively retain during in-line gas sampling. The initial temperature will be held at 35°C and 1 ml of sample will be injected using a 1 ml gas-tight syringe. The initial temperature will be held for 1 minute and the temperature will be raised at 15°C/min up to 245°C. The final temperature will be held for 5 minutes.

All of reactor/transfer line systems including pyroprobe chamber and sample insert probes used in the Phase III analyses will be appropriately packaged and stored for the future analysis.

effluent will pass through the PUF cartridge for sample collection and 1 ml/min will be directed into the GC column for in-line analysis.

In-line GC-MS Analysis: A HP5890A/5970B series GC-MS with DB-5 MS capillary column (30 m length, 0.25 mm i.d., Agilent Technologies, Inc.) will be used for the phase III study. The initial temperature of GC2 will be held at -60°C and sample will be concentrated at the head of the column for 2 and 2.5 (±5%) min for reactor temperature of 600 and 900°C, respectively. During this time period, PUF combustion effluent sample collection will also take place. Two PUF cartridges will be placed in series as shown in Figure 3. After the sample collection, switching valve 1 will be turned to (1) position in Figure 3 to pressurize the GC column. As soon as pressurization begins, the temperature programming of GC2 will be started. The initial temperature will be held for 1 minute and the temperature will be raised at 10°C/min up to 260°C. The final temperature will be held for 5 minutes. Also after the switching valve 1 is turned to (1) position for the GC column pressurization, the PUF cartridges will be removed from the system. The PUF cartridges will be secured, labeled, and appropriately packaged for next business day delivery to 3M Environmental Laboratory with one blank PUF.

Off-line GC-MS Analysis: After the PUF sampling collection, identical sample collection will be performed using a Tedlar sampling bag. The collected off gas will be sampled within 15 min. of collection and analyzed using HP5890A/5970B series GC-MS with SPEL-Q PLOT (Porous Layer Open Tubular) column (30 m length, 0.53 mm i.d., SUPELCO). The Tedlar bags will be heated to ca. 50 – 60°C to ensure that all of the sulfur compounds that are soluble in the condensed water vapor present in the bag are partitioned into the gas-phase. This column will capture the light compounds ($<C_6$) that the DB-5 MS capillary column may not effectively retain during in-line gas sampling. The initial temperature will be held at 35°C and 1 ml of sample will be injected using a 1 ml gas-tight syringe. The initial temperature will be held for 1 minute and the temperature will be raised at 15°C/min up to 245°C. The final temperature will be held for 5 minutes.

All of reactor/transfer line systems including pyroprobe chamber and sample insert probes used in the Phase III analyses will be appropriately packaged and stored for the future analysis.

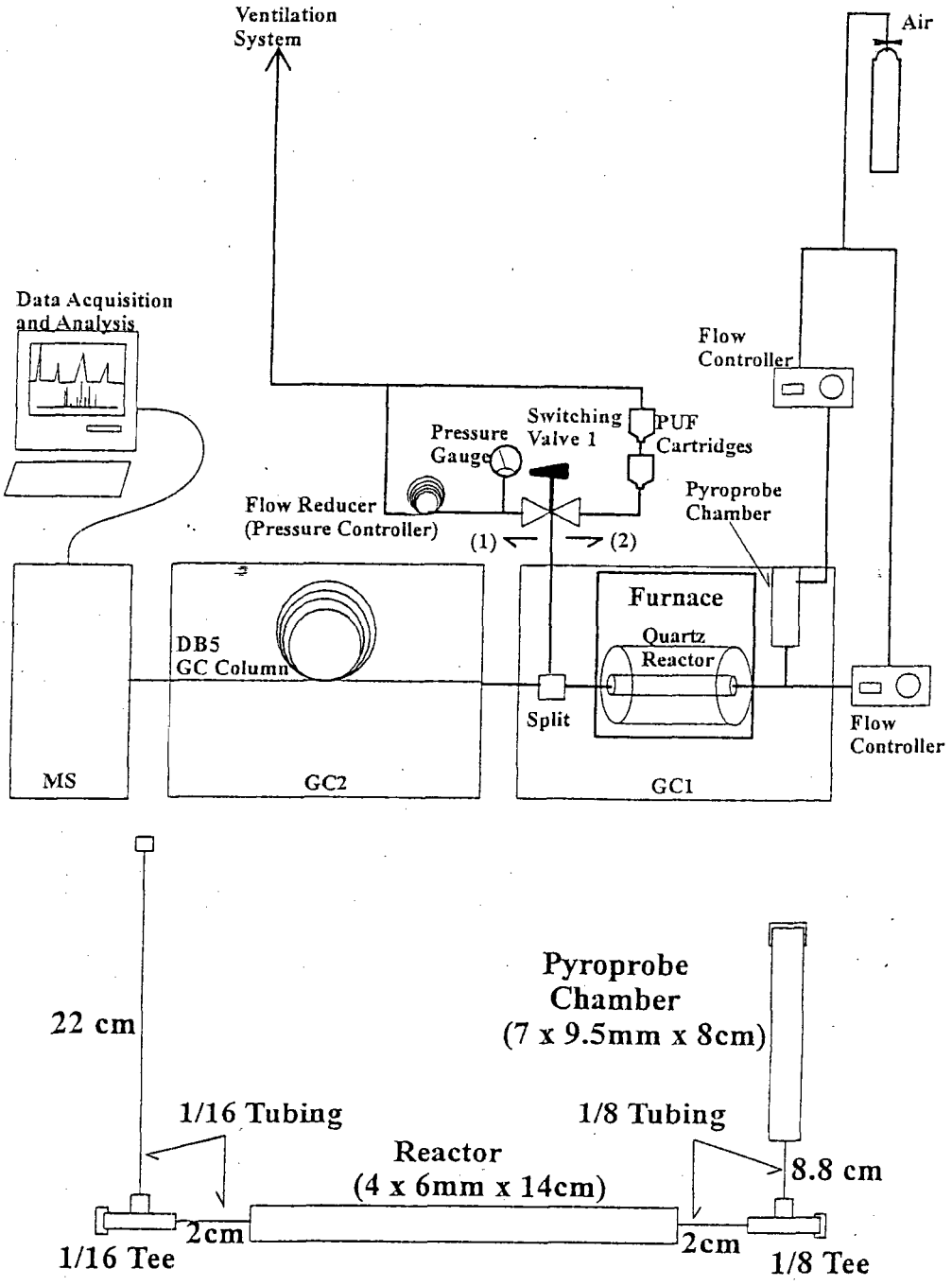

Figure 3. Experimental setup for heated blank sample analysis and collection. Dimensions of the reactor and transfer lines are also shown in lower drawing.

4. Combustion Tests of Seven Selected Compounds

Combustion tests for the seven selected compounds will be performed after the heated blank analysis. Similar to the heated blank analysis, the sample combustion tests will be conducted for the reactor temperature of 600 and 900°C, and the sample collection will be performed twice for

each temperature (one for PUF sample collection and one for the Tedlar bag sample collection). The same analytical tests will be conducted as for the heated blank analyses. After the gas phase analysis and collection, the reactor will be cut in half and extraction of condensed phase products will be performed using the method previously outlined in Section 2 and 3.

Figure 4 shows the schematic diagram of the experimental setup to conduct effluent in-line GC/MS analysis and PUF sample collection for the combustion test of the selected compounds. For off-line GC-MS analysis, the PUF cartridges in Figure 3 will be replaced by a Tedlar bag. Air and methane (if necessary) will be introduced into the pyroprobe chamber and the reactor to simulate incineration of the samples. The flow rate of He and air will be controlled by a flow controller (Porter Flow Instruments, DFC1400) and methane will be introduced using a calibrated syringe pump (KDS101, kdScientific). Because the methane flow rate is very low, it is necessary to use syringe pump to obtain accurate flow rates. The solid and liquid phase samples will be gasified using a pyroprobe (Chemical Data Systems, Model 120) and mixed with air and methane (if necessary) in the pyroprobe chamber. The temperature and the duration time of ignition will range from 1000 to 1250°C and 20 to 40 seconds, respectively, depending on the actual sample being gasified. The gasified mixture will be mixed with the air stream and undergo incineration in the fused silica reactor. A portion of the effluent (1 ml/min) will be delivered to the GC-MS for product analysis and rest of effluent will be passed through two PUF cartridges for detection of PFOS and/or PFBS using LC/MS analysis at 3M environmental laboratories. Further details are provided below.

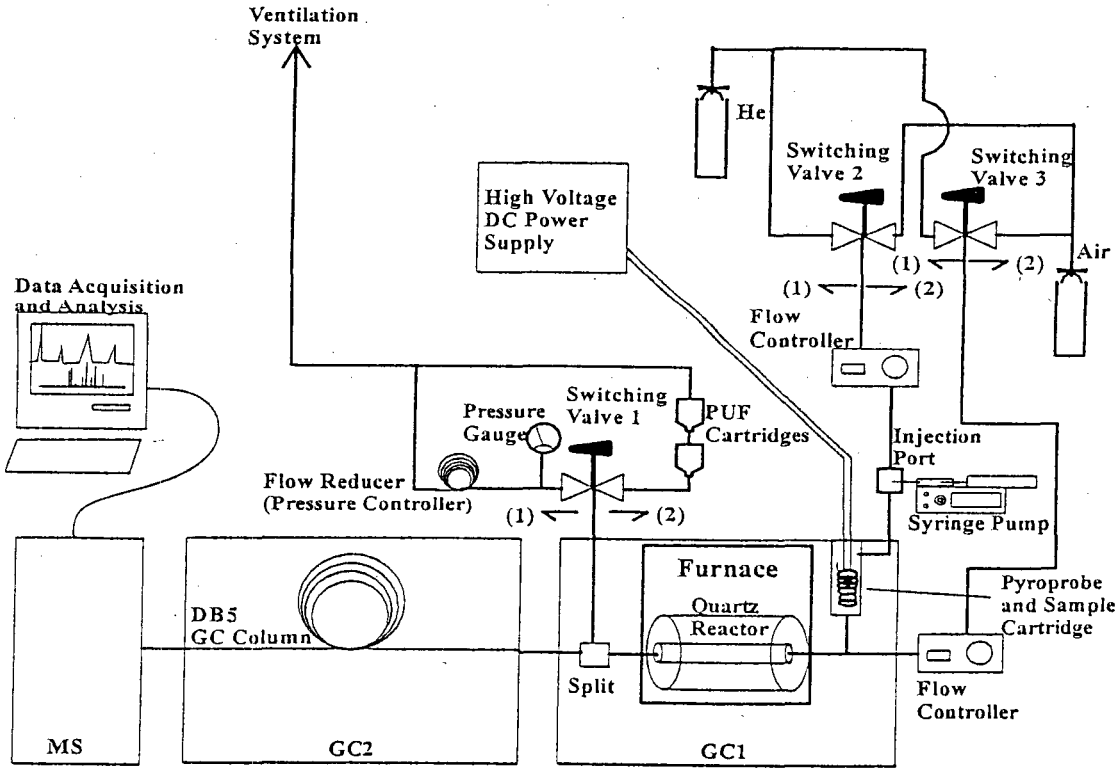

Figure 4. Experimental setup for the combustion tests.

1. Stoichiometric Reaction Mechanisms of Seven Samples

Based on the elemental formula of the seven samples provided by 3M, four of which are normalized by carbon, stoichiometric equations were developed and the amount of necessary oxygen was calculated. The results are tabulated in Table 1. In the development of the stoichiometric equations, it is assumed that C is converted to CO_2, F is converted to HF, N is converted to N_2, and S is converted to SO_2. Phosphorous and potassium were excluded from the equation since the contribution of these elements is very small and their effects on the overall stoichiometry are small enough to be safely ignored. Methane is also introduced for hydrogen deficient samples to supply hydrogen to convert F to HF. In that case, additional oxygen was supplied to convert C in methane to CO_2.

Table 1. Coefficients of Stoichiometric Combustion of Selected Samples

Atomic Contents of Samples									Stoichiometric Gas		Products				
Sample	C	H	F	N	O	P	S	K	O_2	CH_4	CO_2	H_2O	HF	SO_2	N_2
PFBS	4	0	9	0	3	0	1	1	5.5	2	6	0	8	0.5	0
PFOS	8	0	17	0	3	0	1	1	11.5	4	12	0	16	1	0

From the table above, stoichiometric equations can be derived for all of the samples as shown below.

For

2. Calculation of Necessary Amount of Sample (Equivalent Amount of Fluorine in PFOS)

The amount of sample that will be incinerated was calculated to conserve the same amount of fluorine for each sample and is tabulated in Table 2. All samples have the equivalent amount of fluorine that is contained in 0.50 mg of PFOS. To facilitate calculations, we define a "pseudo-molecular weight" to be the sum of the masses of the elements in the empirical formulation of each product as given in Table 1. For example, the pseudo-molecular weight of

The amount of air necessary for stoichiometric incineration for each sample was also calculated and is included in Table 2.

Table 2. Amount of Sample That Contains Equivalent Amount of Fluorine in 0.5 mg of PFOS

Sample Name	(Pseudo) Molecular Weight (g)	Fluorine Fraction by weight	Mass of Sample to be incinerated (mg)	Amount of Air for Stoichiometric Incineration (ml)
PFBS	338	0.506	0.59	1.33
PFOS	538	0.600	0.50	1.38

[a,b] Values in parenthesis will be used for the actual combustion test. See sample amount adjustments. [c]

For example, the amount of that contains equivalent amount of fluorine in 0.5 mg of PFOS can be calculated as:

and the amount of air for stoichiometric incineration can be calculated as:

The necessary amount of sample and air for other six compounds can be calculated in a similar manner.

3. Sample Amount Adjustments

Since FC-1395 and FC-807A were provided in aqueous solution (water contents of 74 and 78 % by weight, respectively), the amount of sample to be loaded will be 2.19 and 2.63 mg, respectively. also contains 10 % (by weight) impurity and the necessary amount that has the equivalent amount of fluorine in 0.5 mg of POSF will be 16.38 mg. This mass of material is approximately one magnitude larger than the other compounds and combustion of such a large mass is beyond the capability of our laboratory-scale apparatus. One-third of the necessary mass is the maximum amount that can be incinerated and satisfy near-stoichiometric combustion and a residence time of 2 s.

4. Sample Loading Method

will be placed directly into the sample probe (1 × 2 mm (i.d. × o.d.) × 2 cm length). FC-1395 and FC-807A, both of which are in aqueous solution, will be placed into a slightly larger sample probe (2 × 4 mm (i.d. × o.d.) × 1.5 cm length) and dried with He and moderate heat (less than 100°C) before being mounted into the

pyroprobe. (The slightly larger sample probe will be used to enhance the drying process.) This process will aid the gasification process by requiring less energy to gasify the active ingredients of the sample. Thermal gravimetric analysis show that significant amounts of mass are lost for both of these samples at temperatures of ca. 150 to 160°C (see Figure 5 and 6). The ratio of the mass at ca. 160°C to the original mass is an indication of the mass lost due to water evaporation. The mass of FC-1395 and 807A before and after this drying process will be measured to confirm that the active ingredients of the sample are not vaporized prior to insertion in the pyroprobe.

$C_4F_9SO_3^-K^+$, and $C_8F_{17}SO_3^-K^+$, which are solid powders, will be placed into the sample probe (1 × 2 mm (i.d. × o.d.) × 2 cm length) with small amount of quartz wool support (0.5 cm in length) in the bottom of the sample probe. The quartz wool is necessary to hold the materials in place prior to the combustion test.

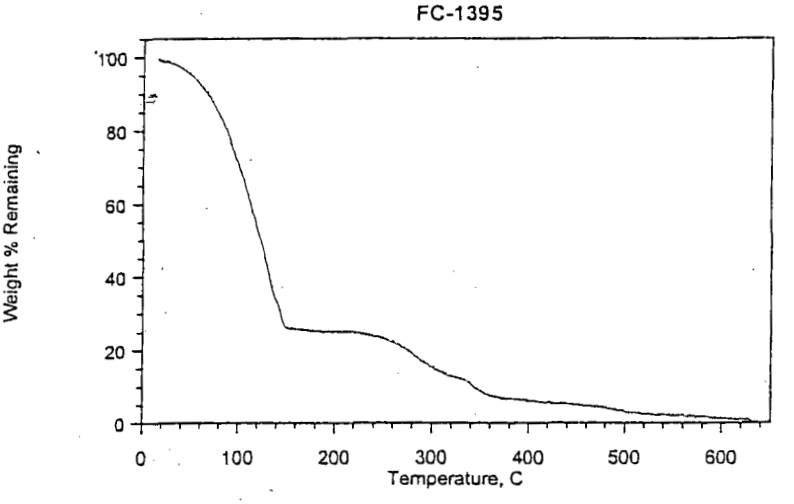

Figure 5. Thermal Gravimetric Analysis (TGA) of FC-1395

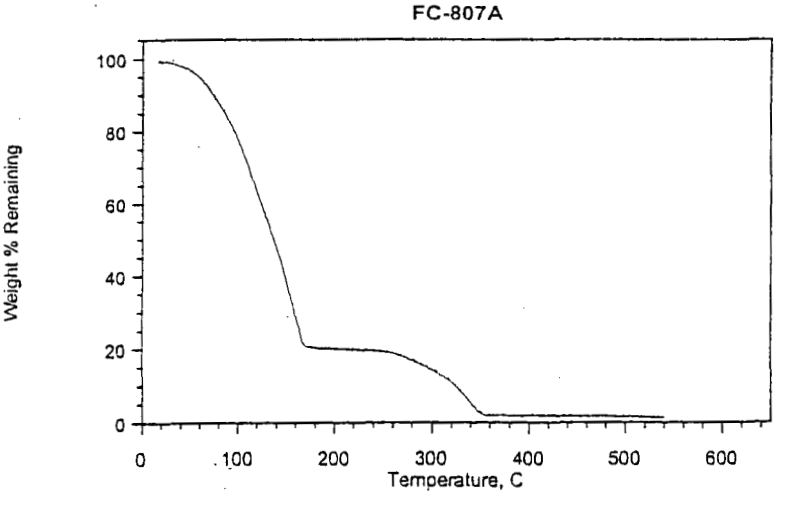

Figure 6. Thermal Gravimetric Analysis (TGA) of FC-807A

5. Experimental Flow Rate Setting and Calculations

Table 3 and 4 summarize the experimental flow settings at temperatures of 600 and 900°C, respectively. The flow rates for He and Air can be controlled within ± 10 %, and the methane flow rate can be controlled within ± 5 %. Because it is necessary to load a large amount for all of available air will be used to obtain near-stoichiometric (ca. 20 % excess air) sample combustion for Other compounds will be incinerated under high excess air condition ranging from ca. 100 to 450 % excess air.

The concentration profile of the gasified sample is not measured directly and assumed to be an average value in the excess air calculations described above. Oxygen and methane-deficient conditions may occur in the reactor during the gasification process for some of the samples while the pyroprobe is heated to high temperatures (1000 to 1250°C) and the volume of the gas expands by a factor of up to 2.5. In other words, during the gasification process, the flow rate of the gasified sample to the reactor may be faster than the calculation shown in Tables 3 and 4. This situation is expected to be most serious for the where the level of excess air is ca. 20%. For the other six samples, the much higher excess air levels infer that oxygen-deficient conditions in the reactor are unlikely to occur.

The calculations shown in Table 3 and 4 are described below with FC-807A as an example. The calculation can be conducted in a similar manner for other six compounds. The numbers in Table 3 and 4 are calculated using a spreadsheet program and the numbers are rounded to the appropriate number of significant digits. Therefore, the calculation may not exactly reproduce the numbers shown in Table 3 and 4.

In Table 3, the necessary amount of CH_4 for FC-807A can be calculated as:

0.58 (mg) × 0.001 (g/mg) / 51.6 (g/mol) × 0.106 (stoichiometric CH_4 requirement, see Table 1) × 0.0821 (atm L / (mol K) × 298 (K) / 1 (atm) × 1000 (ml/L) = 0.03 ml

The necessary amount of CH_4 was then doubled to provide an excess of hydrogen atoms to scavenge fluorine atoms as HF.

The CH_4 flow rate and sweeping time through the pyroprobe were calculated as shown below:

0.06 (ml) / 1.00 (min) = 0.06 (ml/min)

The air flow rate to pyroprobe was added to sweep the sample out of the volume in 1 min. The volume of pyroprobe is 1.5 ml (0.35^2 ×3.14 (cm^2) × 4.5 cm – 0.2 (cm^3). The necessary flow rate to sweep the sample out of the volume at 260°C is:

1.5 (ml) / 1 (min) × 298 (K) / (260 + 273) (K) = 0.84 ml/min

Table 3. Experimental Conditions at 600°C

Sample	Stoichiometric Amount of Air for Sample (ml)	Amount of CH_4 as H Source (ml) (necessary amount × 2)	Sweeping Time (min)	Air Flow Rate to Pyroprobe (ml/min)	CH_4 Flow Rate to Pyroprobe (ml/min)	Air Flow Rate to Reactor for Sample Combustion (ml/min)	Air Flow Rate to Reactor for CH_4 Combustion (ml/min)	Additional Air Flow (ml/min)	Total Gas Flow (ml/min)	Residence Time (s)	Excess Air (%)
FC-1395	1.50	0.02	1.00	0.82	0.02	1.50	0.15	8.00	10.49	1.96	485
FC-807A	1.37	0.06	1.00	0.78	0.06	1.37	0.57	7.50	10.28	2.00	387
PFBS	1.33	0.22	1.00	0.62	0.22	1.33	2.07	6.00	10.24	2.01	176
PFOS	1.38	0.21	1.00	0.63	0.21	1.38	1.98	6.00	10.20	2.02	179

Table 4. Experimental Conditions at 900°C

Sample	Stoichiometric Amount of Air for Sample (ml)	Amount of CH_4 as H Source (ml) (necessary amount × 2)	Sweeping Time (min)	Air Flow Rate to Pyroprobe (ml/min)	CH_4 Flow Rate to Pyroprobe (ml/min)	Air Flow Rate to Reactor for Sample Combustion (ml/min)	Air Flow Rate to Reactor for CH_4 Combustion (ml/min)	Additional Air Flow (ml/min)	Total Gas Flow (ml/min)	Residence Time (s)	Excess Air (%)
FC-1395	1.50	0.02	1.30	0.63	0.01	1.15	0.12	5.80	7.72	1.99	457
FC-807A	1.37	0.06	1.30	0.60	0.05	1.05	0.44	5.50	7.63	2.01	369
PFBS	1.33	0.22	1.30	0.48	0.17	1.02	1.59	4.50	7.76	1.97	172
PFOS	1.38	0.21	1.30	0.48	0.16	1.06	1.53	4.50	7.73	1.98	174

Since 0.06 ml/min of 0.84 ml/min is provided by CH_4, the air flow rate will be 0.84 – 0.06 = 0.78 ml/min.

The necessary air flow rate to the reactor for sample combustion can be calculated by the stoichiometric amount of air for sample and sweeping time:

1.37 (ml) / 1 (min) = 1.37 ml/min

The stoichiometric combustion ratio of methane to air is 1 : 9.57. Therefore the air flow rate to reactor for CH_4 combustion can be calculated as:

0.06 ml/min × 9.57 = 0.57 ml/min

With the additional air flow rate shown in Table 3, the total gas flow rate is calculated as 10.28 ml/min.

The residence time for 0.4 cm i.d. x 8 cm effective length quartz tubing at 600°C is calculated as:

$0.2^2 \times 3.14 \times 8$ (ml) / [10.28 (ml/min) / 60 (s/min) × (600 + 273) (K) / 298 (K) = 2.00 s.

The excess air ratio is the ratio of additional air to stoichiometric air. For FC-807A, 7.5 ml/min additional air flow will be introduced while 1.94 ml/min is the air flow rate for stoichiometric combustion (sample + CH_4). The excess air ratio is calculated as:

7.5 (ml/min) / 1.94 (ml/min) × 100 = 387 %

6. Effective Length of Reactor

The effective length of the reactor was determined based on measured temperature profiles at 600 and 900°C. The temperatures of reactor wall (outside) were measured by thermocouples (Chromel-Alumel Type K, 304 SS Sheath, OMEGA) wrapped with quartz tape to prevent radiation effects from the heater. For the reactor temperature of 600°C, the temperature was set at 613°C. The effective length of 8 cm was obtained by allowing a deviation from the desired temperature (600°C) by ± 20°C, which is ± 3.3 % of desired temperature. The measured temperatures at the center of the reactor and at a distance of 1, 2, 3, 4, and 5 cm from the center are shown in Figure 7. For the reactor temperature of 900°C, temperature was set at 928°C. The 8 cm effective length was obtained by allowing a deviation from the desired temperature (900°C) by ± 30°C, which is also ± 3.3 % of desired temperature. The measured temperatures at the center of the reactor and at a distance of 1, 2, 3, 4, and 5 cm from the center are also shown in Figure 7.

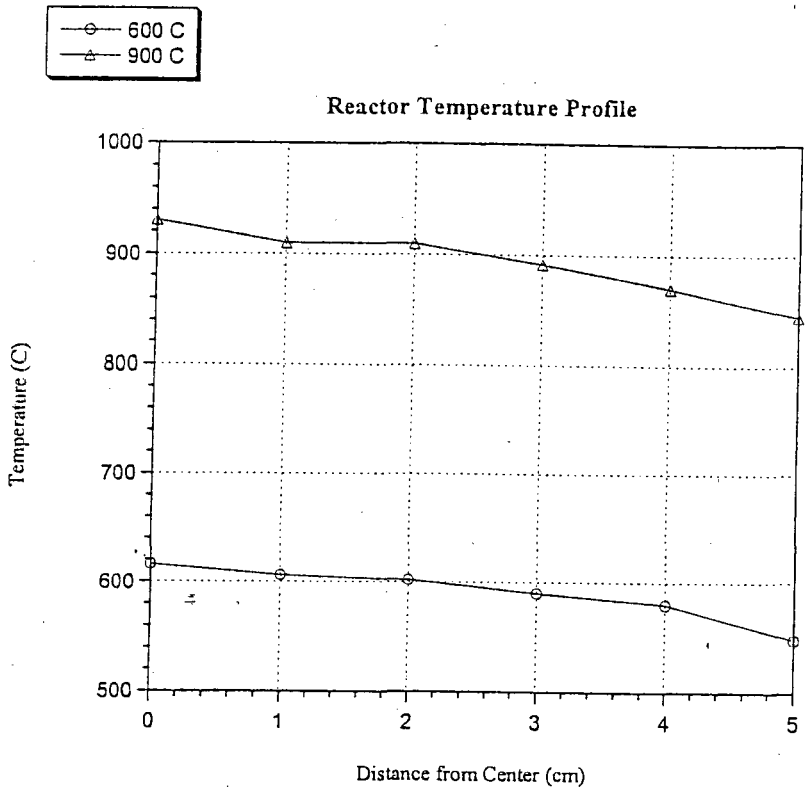

Figure 7. Reactor Temperature Profile for 600 and 900°C.
The profiles are roughly symmetrical about the center of the reactor.

7. Experimental Procedure (Gas Phase Sample Analysis and Collection)

Helium will be used initially to purge both air and methane lines to the pyroprobe and reactor/transfer line. The experiments start with setting the flow rate of air and methane and the temperatures of GC1 (260°C), furnace (600 or 900°C), and the GC2 (-60°C). After the temperature is appropriately set, air and methane, if necessary, will be introduced into the pyroprobe, and air will be introduced into the reactor. The exhaust gas will be vented without pressurization by setting the switching valve 1 to (2) position. The pyroprobe will not be mounted initially in the system, instead the top of pyroprobe chamber will be capped. The sample will be carefully loaded into capillary quartz tubing, 1mm (i.d.) × 2mm (o.d.) × 2.0 cm (length) or 2mm (i.d.) × 4mm (o.d.) × 1.5 cm (length), the net weight of sample measured, and the tubing carefully inserted into the pyroprobe. After the flow rate and temperature are properly set and sample preparation is completed, the system will be held for 1 minutes to allow the flow to stabilize. The cap for the pyroprobe chamber will then be removed and the pyroprobe quickly inserted into its chamber. Immediately afterwards, the pyroprobe will be ignited to gasify the sample. After the appropriate amount of time to sweep the gasified sample from the pyroprobe chamber (1.2 times of sweeping time shown in Table 3 and 4), the air flow for the pyroprobe will be maximized (5 ml/min at room temperature, 8.9 ml/min at 260°C) and held for 10 s. The switching valve for both the pyroprobe and reactor will then be switched to helium. After approximately 20 sec, switching valve 1 will be turned to (1) position to pressurize the GC

column. As soon as the column pressurization is started, GC temperature programming and MS analysis will be started. The temperature programming will be identical to that described in Section 3 (Heated Blank Combustion Test). The PUF cartridges will be also removed from the system. The PUF cartridges will be secured, labeled, and appropriately packaged for next business day delivery to 3M Environmental Laboratory with one blank PUF. The same experiment will be repeated for the sample collection using a Tedlar bag. The sampling method and off-line GC-MS analysis will be identical to the heated blank analysis described in Section 3. Since the same reactor will be repeatedly used for two combustion temperatures, the blank analysis will be performed between each analysis to examine any carryover from the previous analysis. The exhaust gas will be vented to a laboratory hood following each test (as shown in Figure 5) to minimize any cross contamination during Phase III study.

8. **Experimental Procedure (Condensed Phase Sample Extraction)**

After gas-phase and PUF sample collection and analysis are completed, condensed phase sample extraction will be performed. This process will be identical to Section 2 - Laboratory Spike Analysis, as illustrated in Figure 2. The collected samples will be secured, labeled, and appropriately packaged for next business day delivery to 3M Environmental Laboratory with one blank vial (40 ml) containing 5.5 ml methanol. The sample probe (capillary quarts tubing) used for sample loading will be weighed after the combustion test to determine the net amount of sample gasified.

5. Transfer Efficiency Test for $C_4F_9SO_3^-K^+$, and $C_8F_{17}SO_3^-K^+$

Figure 8 shows schematic diagram of transfer efficiency test for $C_4F_9SO_3^-K^+$, and $C_8F_{17}SO_3^-K^+$. The starting materials will be collected using two PUF cartridges in the same manner as described earlier for the combustion tests, however, in these tests, the furnace temperature will be held at 260°C. The helium flow rate will be set as 20 ml/min and the temperature in the GC oven will be set as 260°C. The sample preparation and loading processes are the same as the combustion off-gas collection. The switching valve, which is originally set to (2) position in Figure 8, will be switched to (1) position just before the pyroprobe/sample insertion. The sample will be collected for two minutes after gasification begins. The collected samples will be secured, labeled, and appropriately packaged for next business day delivery to 3M Environmental Laboratory with one blank PUF.

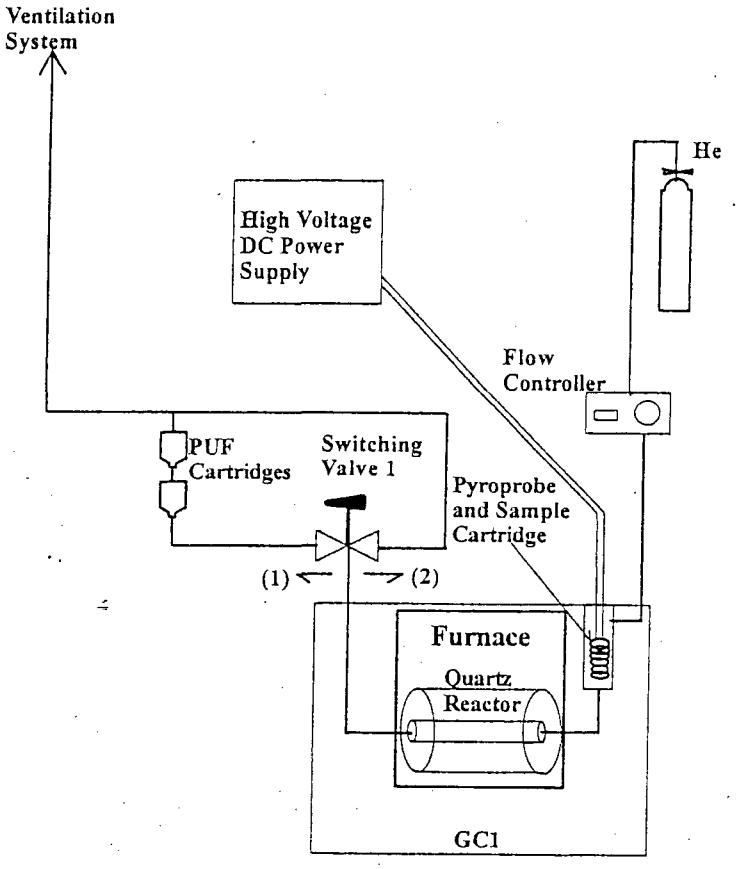

Figure 8. Transfer Efficiency Test for , $C_4F_9SO_3^-K^+$, and $C_8F_{17}SO_3^-K^+$

6. Cross Contamination Prevention and Examination

Extensive precautions will be applied to minimize any PFOS/PFBS cross-contamination due to the release of these environmentally persistent materials into the immediate laboratory environment following each combustion test. The effluent exhaust line has been connected to a laboratory hood in KL 112 following the results of the phase II study to mitigate the release of PFOS/PFBS into the immediate laboratory environment associated with the off-line PUF sample collection. Prior to Phase III study, the laboratory tabletop and STDS combustion apparatus will be completely cleaned using reagent grade methanol and acetone and only the cleaned tabletop will be used for sample preparation and system assembly and disassembly. After the first cleanup of the desktop, the surface will be wiped using 3M Scotch-Brite High Performance Cloths with HPLC grade methanol that is used for sample extraction. The cloth will be soaked with methanol and squeezed before each wipe test. The wiping methods will follow 3M's instruction given at previous laboratory wipe test. The wiped cloth will be stored in the I-CHEM 40 ml vial provided by 3M. The vial will be stored outside of the KL 112 where the Phase III study will be conducted. The cleaning and wipe tests will be conducted following the completion of each subsection task and between each sample if the section involved multiple sample analysis.

7. Samples to be sent to 3M

The following samples will be sent to 3M Environmental Laboratory for each test shown in Figure 1 excluding test 1. Blanks for PUF, solvent, and wipe test will be included in each shipment whenever these analyses/collection are performed. Next business day delivery will be used for all shipments. Eleven total shipments are scheduled. The contents for each shipment to be delivered are as follows:

Test 2 ----- Two extracts (5.5 ml) for each test compound (PFOS and PFBS), one solvent blank (5.5 ml), one wipe test, and one wipe test blank

Test 3 ----- Two sampled PUF cartridges, one blank PUF cartridge, two extracts (5.5 ml), one solvent blank (5.5ml), two wipe test, and one wipe test blank

Test 4 ----- Four sampled PUF cartridges [two for 600°C (1^{st} and 2^{nd} collections) and two for 850°C (1^{st} and 2^{nd} collections)], one blank PUF, two extracts (5.5 ml) (1^{st} and 2^{nd}), one solvent blank (5.5 ml), two wipe tests, and one wipe test blank [Samples listed above are for each test compound. There are seven test compounds in Test 4.]

Test 5 ----- Two sampled PUF cartridges, one blank PUF cartridge, two extracts (5.5 ml), one solvent blank (5.5ml), two wipe test, and one wipe test blank

Test 6 ----- Two sampled PUF cartridges (1^{st} and 2^{nd}) for each test compounds $C_4F_9SO_3^-K^+$, and $C_8F_{17}SO_3^-K^+$), one blank PUF cartridge, two wipe tests, and one wipe test blank

8. Changes in Original Protocol

Three significant changes have been made as the experimental approach has evolved after the original proposed protocol was approved by EPA. They are outlined below.

1. Significant changes were made to the sample inlet and gasification system. To satisfy the analytical requirements for PFOS/PFBS detection by LC/MS analysis by 3M, we determined that relatively large amounts of sample, 0.5 to several mg, had to be gasified in the actual experiments. This amount of sample is much larger than initially estimated (ca. 10 to 100 μg) and could not be gasified with the inlet available with the Advanced Thermal/Photolytic Reactor System (ATPRS). Preliminary experiments in phase II also demonstrated that higher gasification temperatures (> 400°C) were necessary to rapidly gasify the fluorocarbon-based samples. As such, the System for Thermal Diagnostic Studies (STDS), equipped with a high-temperature pyroprobe that can gasify milligram quantities of material, is proposed for the phase III combustion tests. The STDS is very similar to the ATPRS with regard to its incineration/analytical capabilities and is a satisfactory substitute for the ATPRS.

2. In the approved protocol, we had originally planned sample combustion with hydrocarbon fuels (e.g., n-octane) for all of samples. Subsequently, it was determined that a substitute was need because the liquid hydrocarbon fuels originally proposed require much larger amount of oxygen (air) to obtain stoichiometric oxidation and it is impossible to maintain the residence time of 2 seconds in the reactor under stoichiometric or excess air environments. Methane has the lowest chemical oxygen demand of any hydrocarbon fuel and is a satisfactory replacement. We propose to use methane as a fuel if the sample is hydrogen deficient and requires hydrogen source to convert F to HF, otherwise fuel will not be introduced to the reactor.

3. In the approved protocol, we also proposed to conduct combustion tests at three temperatures (600, 750, and 900°C). Preliminary combustion tests with several samples indicates that many combustion byproducts were formed at 600°C, but those combustion byproducts were not observed at higher temperature (750 and 900°C) and the GC-MS total ion chromatograms for these higher temperatures were very similar. Therefore it is proposed that two temperatures are sufficient to analyze the combustion phenomena of the selected samples (600 and 900°C).

November 4, 2002

Addenda for Phase III Protocol

9. 2nd Transfer Efficiency Test for $C_4F_9SO_3^-K^+$ (PFBS), and $C_8F_{17}SO_3^-K^+$ (PFOS)

In addition to the transfer efficiency tests specified in phase III protocol, direct transfer efficiency tests where the gasified samples are collected without passing through the combustion reactor will also be performed. Samples will be collected using two PUF cartridges. Extraction of the entire system (pyroprobe chamber and transfer tubing) will be performed using methanol as the solvent. This additional study will provide information concerning how much PFBS and PFOS is transported from the pyroprobe through the transfer lines to the reactor entrance. The transfer efficiency tests in the phase III protocol address sample transport from the pyroprobe to the combustion reactor exit.

Figure 9 shows a schematic diagram of the direct transfer efficiency test for PFBS, and PFOS. The gasified samples will be collected using two PUF cartridges in the similar manner as described in Section 5 of the phase III protocol. The PUF cartridges will be directly connected to the pyroprobe chamber by 19.5 cm long, 1/8" o.d. Silcosteel tubing (Silcosteel, Restec, Inc.). The GC oven temperature will be held at 260°C through the entire analysis. The detailed flow profiles are shown in Table 3. Helium will be used as a carrier gas. The flow will be set as 0.63 ml/min and held for one minute before the sample is inserted and gasified. After the sample is placed in the pyroprobe, the flow will remain at 0.63 ml/min for 94 seconds while the sample is gasified at 1250°C for 40 seconds. The flow rate will then be maximized to 4.53 ml/min and held for 30 seconds to purge the sample from the pyroprobe chamber and transfer line. The conditions and operational procedures were determined to simulate gas-phase combustion of , PFBS, and PFOS at 600°C.

The calculated entire volume is 3.79 ml as shown the detail below:

Pyroprobe chamber:	$(0.35)^2$ (cm^2) × 3.14 × 8 (cm)	= 3.08 ml
Transfer line:	$(0.108)^2$ (cm^2) × 3.14 × 19.5 (cm)	= 0.71 ml
Total:		3.79 ml

The system will be extracted with methanol using five times the volume of the pyroprobe and heated transfer lines (19.0 ml). Prior to the extraction, the sample probe and pyroprobe will be removed from the system. The collected samples will be secured, labeled, and appropriately packaged for the delivery to 3M Environmental Laboratory with a methanol solvent blank.

Table 3. Flow Rate Profile for Direct Transfer Efficiency Test

Time Period (sec)	Pyroprobe Flow Rate (ml/min)	Volume (ml)
0 – 60	0.63	0.63
60 – 85	0.00[a]	0.00
85 – 179	0.63	0.99
179 – 189	0.63 → 4.53[b]	0.43
189 – 219	4.53	2.27
	Total Volume (ml)	4.32

[a] No flow due to open system to insert the sample.
[b] Linear increase (approximate)

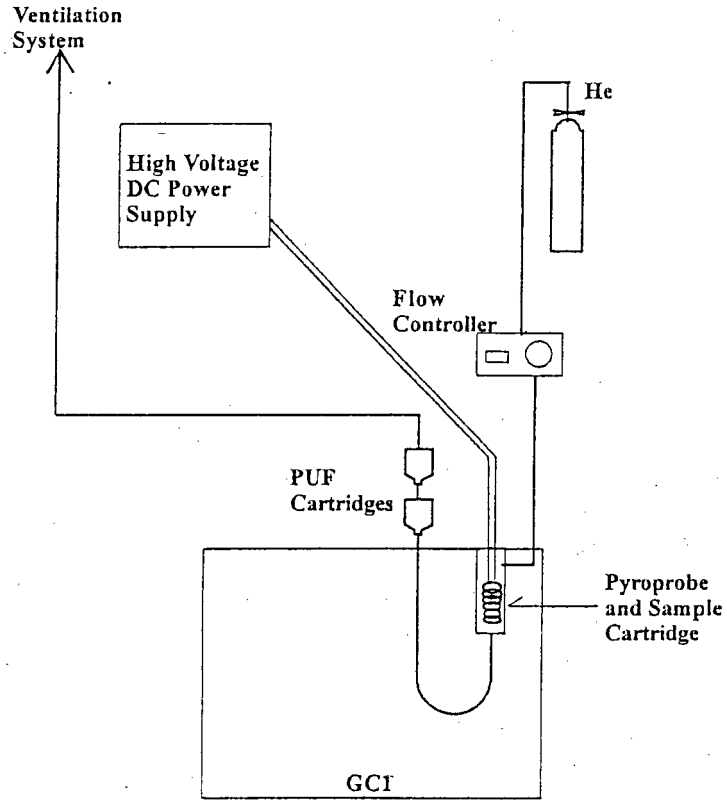

Figure 9. Direct Transfer Efficiency Test for , PFBS, and PFOS.

10. Additional Extraction Analysis of Unheated Sample Transport Lines

In addition to the extractions specified in the phase III protocol, the unheated sample transport lines downstream of the combustion furnace (switching valve and the transfer line between switching valve and PUF cartridge) will be extracted using methanol. This analysis will be performed for FC-807A and PFOS after the combustion tests at 600°C. This analysis will determine if PFOS/PFBS condensation occurs while the effluent is being collected using ambient temperature PUF sampling cartridges.

The method will be similar to other extraction analysis. The measured volume of the unheated transport line is 0.55 ml. The line will be extracted with methanol using a volume equal to 5 times the transport line volume (2.75 ml). The collected samples will be secured, labeled, and appropriately packaged for the delivery to 3M Environmental Laboratory with a methanol solvent blank.

11. Blank Combustion Analysis Using Single PUF between 600 and 900°C Combustion Test.

After combustion tests of the first three samples were completed, we decided to perform another blank combustion analysis using a single PUF after the combustion test at 600°C but before the combustion test at 900°C for the rest of the samples (FC-807A, , PFBS, and PFOS). The temperature of the GC oven and reactor will be set at 260 and 600°C, respectively. Table 4 shows the flow profile that will be performed for this analysis.

Table 4. Flow Rate Profile for PUF Collection (Blank Analysis between 600 and 900°C)

Time Period (sec)	Reactor Flow Rate (ml/min)	Pyroprobe Flow Rate (ml/min)	Total Flow Rate (ml/min)	Volume (ml)
	Air	Air		
0 – 120	9.70	0.84	10.54	21.08
120 – 130	9.70	0.84 → 4.63[a]	10.54 → 14.33	2.07
130 – 140	9.70	4.63	14.33	2.39
140 - 160	8.89 (He)[b]	4.53 (He)[c]	13.42	4.47
			Total Volume (ml)	30.01

[a] Linear increase (approximate). [b,c] Switched to helium for sweep

Air and helium will be used for the sample collection. The flow rate for the reactor and the pyroprobe will be same as the actual combustion test at 600°C. Air will flow for 120 seconds and then increased to the maximum flow rate and held for 10 seconds. Air will be replaced by helium to purge all the air from the system for 20 seconds. The collected samples will be secured, labeled, and appropriately packaged for the delivery to 3M Environmental Laboratory with the other PUFs and methanol extractions.

12. 3rd Transfer Efficiency Test for PFBS and PFOS (Sample in Reactor)

Another transfer efficiency test where PFBS and PFOS are directly placed in the reactor and gasified will also be conducted. This analysis will demonstrate the PFBS/PFOS transport efficiency of the overall system downstream of the combustion reactor. It will also demonstrate how efficiently the PUFs capture the PFBS and PFOS that exits the reactor in the vapor/aerosol phase. Figure 10 shows a schematic diagram of 3rd transfer efficiency test. GC/MS in-line analysis, sample collection using PUF, off-line GC/MS analysis using Tedlar bag, and reactor/transfer line, valve extraction using methanol will be performed in this study using air and helium as carrier gases. A detailed analytical procedure follows.

1. PUF collection and in-line GC/MS analysis for PFBS gasification with air.

2. Tedlar Bag Collection and off-line GC/MS analysis for PFBS gasification with air.

3. Methanol extraction for PFBS gasification with air.

4. PUF collection and in-line GC/MS analysis for PFBS gasification with He.

5. Tedlar Bag Collection and off-line GC/MS analysis for PFBS gasification with He.

6. Methanol extraction for PFBS gasification with He.

7. PUF collection and in-line GC/MS analysis for PFOS gasification with air.

8. Tedlar Bag Collection and off-line GC/MS analysis for PFOS gasification with air.

9. Methanol extraction for PFOS gasification with air.

10. PUF collection and in-line GC/MS analysis for PFOS gasification with He.

11. Tedlar Bag Collection and off-line GC/MS analysis for PFOS gasification with He.

12. Methanol extraction for PFOS gasification with He.

The sample will be loaded into a sample probe and placed in the middle of the reactor. The gasification temperature will be determined based on the TGAs conducted in the development of the Phase I test protocol. The transfer lines will be heated to 260°C and then the reactor will be heated to the appropriate temperature. The reactor temperature will be between 525 and 575°C depending on the sample and carrier gas. The temperature will be held for 5 minutes for sample collection and in-line GC/MS analysis. The PUF collection, in-line GC/MS analysis and off-line GC/MS analysis will be performed in the similar manner as described in Section 5 of the phase III protocol. The flow rate will be set as 10.8 ml/min to maintain the sample retention time in the reactor at approximately 2 seconds.

The calculated reactor volume and measured valve/transfer line volume are 1.82 and 0.21 ml, respectively, yielding a total volume of 2.03 ml. The reactor/transfer line, valve system will be extracted by methanol using a volume equal to 5 times the volume of the reactor/transfer line, and valve (10.2 ml). Prior to the extraction, sample probe will be removed from the system. The collected samples will be secured, labeled, and appropriately packaged for the delivery to 3M Environmental Laboratory with a methanol solvent blank.

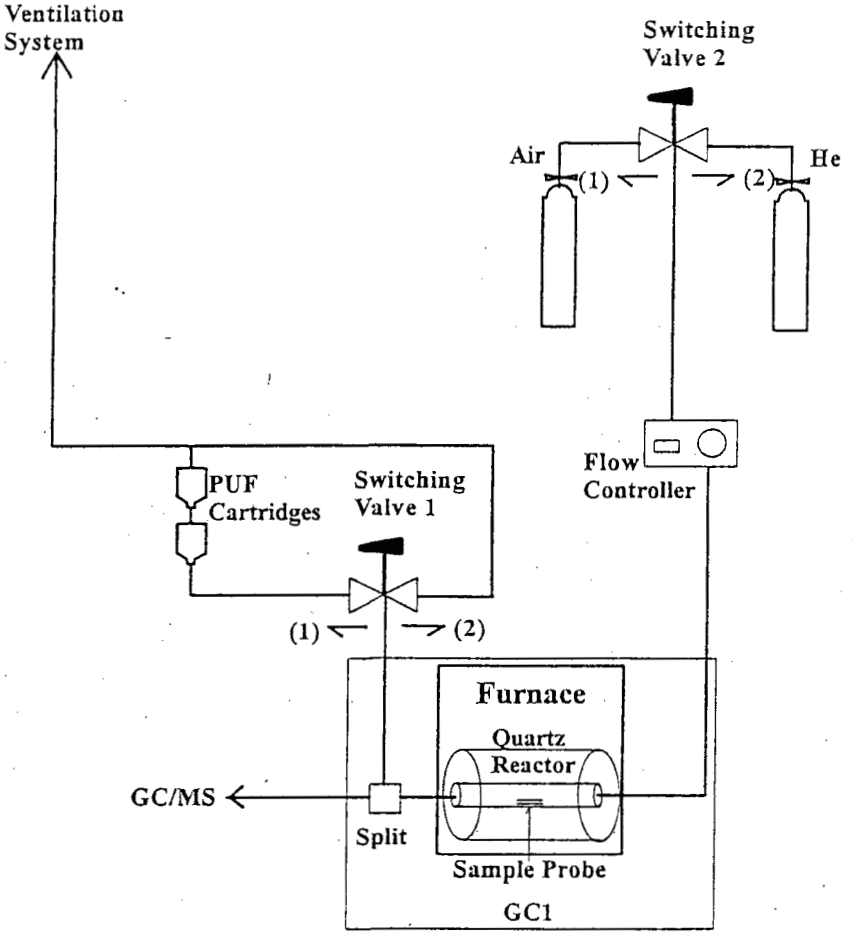

Figure 10. Schematic Diagram of 3rd Transfer Efficiency Test

13. Sulfur Recovery Analysis

Sulfur recovery rate as SO_2 using the in-line GC/MS system was not quantitatively repeatable. This was due primarily to the low SO_2 peak resolution using the cryogenic focusing method at -60°C with a holding time of ca. 4 min. Because the SO_2 peaks using the off-line GC/MS system were much sharper than those observed using in-line GC/MS, we decided to use off-line GC/MS analytical results to quantitatively analyze the sulfur recovery analysis as SO_2. This section describes the overall protocol for these tests.

13.1 Calibration Curve

Pure sulfur dioxide (Aldrich 99.9+ %) will be diluted to 100, 400, 700, 1000 ppm using the Tedlar bag (SKC Inc., 0.5 L) to construct the calibration curve. The column and the GC/MS operating conditions will be same as used for off-line GC/MS analysis of the actual combustion tests. Each concentration will be performed twice and the average will be taken.

13.2 SO_2 Transfer Efficiency Analysis

Known amount of SO_2 standard will be injected into reactor and collected along with carrier gas (air) flow by 0.5 L Tedlar bag. 1 ml of collected sample will be injected to off-line GC/MS system and recovery rate will be calculated using the calibration established above.

Figure 11 shows the schematic diagram of SO_2 transfer efficiency test. The reactor/transfer line system will be heated at 260°C throughout the SO_2 transfer efficiency test. Dry air will be used as a carrier flow. The flow rate for the reactor and pyroprobe will be 8.0 and 0.75 ml/min, respectively. After the switching valve is turned to (1) position, 1 ml of 4.0% concentration SO_2 will be injected to the reactor. The sample will be collected for 2.5 min, then the switching valve will be turned to (2) position and the bag will be closed. The sampled bag will be brought to off-line GC/MS system and 1 ml of sample will be injected. The total amount of molar number in the Tedlar bag will be calculated based on the calibration curve and the total volume collected. The recovery rate will be estimated based on the total amount of molar number collected over the total amount of molar number injected. The test will be conducted twice and the average will be taken.

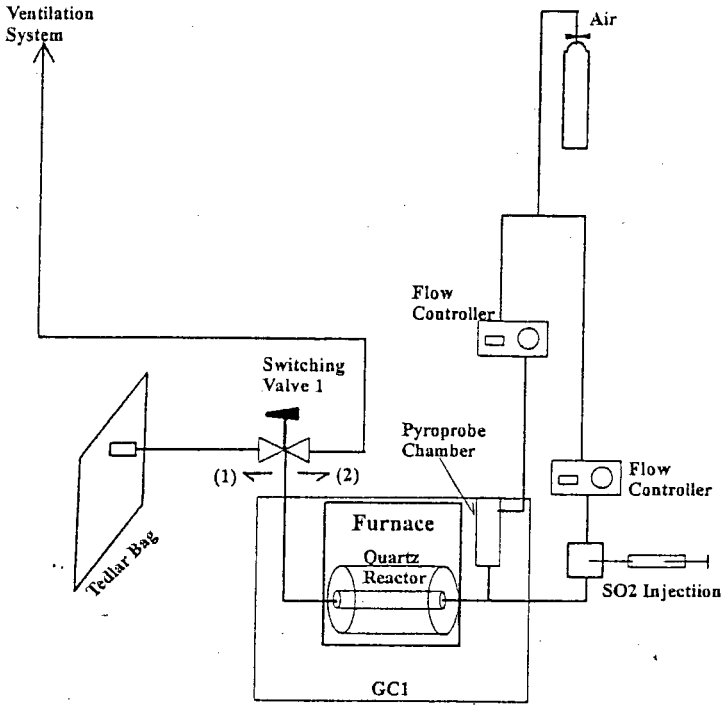

Figure 11. Schematic Diagram of SO_2 Transfer Efficiency Test

Appendix 4

The 3M Analytical Report

Analytical Report

Analytical Results for the University of Dayton Research Institute Study Titled "Laboratory-Scale Thermal Degradation of Perfluoroalkyl Sulfonates and Perfluoroalkyl Sulfonamides"

Combined Laboratory Report for E02-0820, E02-0821, E02-0822,

E02-0839, E02-0840, E02-0867, E02-0895, E02-0896,

E02-0898, E02-0899, E02-0916, E02-0917, E02-0926,

E02-0968, E02-0969, E02-0970, and E02-0971

Testing Laboratory

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1 Introduction

Solvent extracts and polyurethane foam (PUF) cartridges (Supelco, ORBO™-1000, 22mm OD PUF Sampler) were submitted to the 3M Environmental lab to determine at what levels PFOS, PFBS, and were present in the samples generated at the University of Dayton Research Institute, URDI, during the study titled "Laboratory-Scale Thermal Degradation of Perfluoroalkyl Sulfonates and Perfluoroalkyl Sulfonamides". Sample results presented here were generated at 3M using LC/MS instrumentation to detect and quantitate the anions of PFOS ($C_8F_{17}SO_3^-$), PFBS ($C_4F_9SO_3^-$),

Individual study samples and quality control samples are presented in Appendix A, which contains both the measured anion concentrations and the concentration of the compounds uncorrected for purity and the contribution of the potassium cation to the mass used allowing URDI to calculate percent recoveries. The interpretation of results is beyond the scope of this report and will be completed by URDI study personnel and the 3M requester and presented in the URDI final report.

2 Sample Receipt

Reported samples were received at the 3M Environmental Laboratory from URDI between August 20 and September 23, 2002 and analyzed between September 13 and October 8, 2002. The samples consisted of methanol extracts and PUF cartridges. All samples were stored at room temperature in sample check-in until analysis. After a sample was analyzed, the remaining extract or sample was stored in a refrigerator at approximately 4°C. Dates of receipt of all samples are documented in the raw data.

Samples E02-0899-43014 and E02-0899-43012 were not located with the associated samples in sample check-in. These samples were associated with the extraction blank and first extraction for the second heated blank combustion. There are no results reported for these samples.

Three sample containers, I-Chem vials, were received not labeled. It is assumed that these samples correspond to the blank, first and second extraction samples (E02-0840-42716, E02-0840-42714, and E02-0840-42715) for the FC-1395 incineration test, since they were received with the other FC-1395 samples. The individual I-Chem vials associated with these samples were consequently labeled as E02-0840-A, B, and C and were identified as such in the raw data and report.

The wipe samples that arrived with each set of samples were not analyzed but are retained for possible future analysis. All study samples collected but not analyzed will be retained until permission is provided by the requester to discard them in an appropriate manner.

3 Holding Times

Holding times for analysis were not assigned prior to sample receipt. Sampling dates, receipt dates and analysis dates are all documented in the raw data. It is not expected that sample storage conditions at the laboratory would contribute to analyte degradation, especially since study samples were subjected to the thermal degradation study conditions. It is also expected that the fluorochemicals measured are stable in methanol over the time period of this study.

4 Methods - Analytical and Preparatory

Preparatory and analytical methods were not validated for this project but are processed with quality control spikes and blanks to assess method performance. For this project, methanol extracts and polyurethane foam (PUF) cartridges were analyzed via LC/MS. Most of the methanol extracts did not require any further preparation prior to analysis. However, some extracts did require a simple dilution in methanol prior to analysis. These samples (extracts and dilutions) were aliquoted into sample vials and analyzed.

The PUF samples, lab control blanks, and lab control spikes required extraction prior to analysis. In summary, the PUF was extracted by removing the large plastic endcap at the wide end of the cartridge and pushing the PUF with a clean disposable glass pipette until the top was approximately halfway down the cartridge. Then twenty milliliters of methanol was added to the PUF in the cartridge. The large plastic endcap was replaced and the cartridge was vortex mixed for at least fifteen seconds and then inverted five times to ensure proper mixing. Then the sample was allowed to sit for fifteen minutes to allow for desorption of the analytes of interest. After fifteen minutes, the sample was drained and washed again with the same twenty milliliters an additional four times for a total of five washes. After the fifth wash, the methanol was collected and aliquoted into a sample vial for analysis via LC/MS.

Analysis of samples was conducted based on ETS-8-155.1 "Analysis of Waste Stream, Water Extracts or Other Systems Using HPLC-Electrospray/Mass Spectrometry." This method is not written specifically for the extraction of PUF cartridges, just for the analysis of the analytes of interest via LC/MS. The method was modified (documented as deviations) to strengthen the data quality for these analyses by the following: standard curves are to be injected only prior to the samples, CCVs are injected at least every ten samples, the coefficient of determination is to be greater than 0.990, CCVs must be within ±25%, the system suitability must be <5.0% relative standard deviation (RSD) for area counts and <2.5% RSD for retention times, and the standards should be within ±25% (lower limit of quantitation (LLOQ) ±30%) of their true value. Any deviations from this method are discussed in section 5 of this report.

Samples were analyzed on an Agilent 1100 Series LC/MSD in the negative ion mode. Approximate instrument conditions are presented below. Actual conditions are documented in the raw data.

LC CONDITIONS:

Column Flow:	0.300 ml/min	Solvent A:	2 mM Ammonium Acetate
Injection Volume:	3-5 µL	Solvent B:	Methanol
Column Temperature:	30°C	Gradient:	
Column:	Betasil C18		
Column Size:	2x50 mm, 5 µ		

Time	%A	%B
0.00	85	15
0.50	85	15
3.00	0	100
5.50	0	100
6.00	85	15
9.00	85	15

MS CONDITIONS:

Mode:	SIM
Polarity:	Negative
V Cap:	4000 V

SIM Ions:

Compound	Ion
PFOS	499
PFBS	299

5 Analysis

5.1 Calibration

Calibrations curves were constructed using at least five concentrations with quadratic fitting. All coefficients of determination were greater than 0.990 and all calibration standards used in the calibration curves were within ±25%, the LOQ within ±30%. Calibration standards outside this range that were excluded are documented in the raw data along with technical justification for deactivation of curve points. Continuing calibration verification standards (CCVs) were analyzed after no more than 10 samples. All CCV recoveries were within ±25% as specified by the method.

5.2 System Suitability

Out of the ten analytical runs where three compounds in each were evaluated (30 total) all system suitabilities passed for the analytes of interest except for on 9/26/02 (PFBS), 10/04/02 (PFOS), and 10/08/02 (PFBS). The system suitabilities were 5.2%, 5.2%, and 5.3% RSD respectively, exceeding the 5.0% RSD criterion typically allowed. Since all calibration curves and CCVs all passed for each analysis, the data were accepted.

5.3 Blanks

All solvent blanks were less than one half the area counts of the lower limit of quantitation with two exceptions. On 9/30/02, a methanol blank contained approximately 9.4 pg/µL of PFOS. This methanol blank was followed by E02-0895-42975 (PFOS-BLK-PUF), which had PFOS levels below the LLOQ (<5.00 pg/µL). Since the next sample following the blank was <LLOQ, this one time occurrence did not affect the data. Also, on 9/23/02, all of the methanol blanks contained approximately 8-9 pg/µL of Since the instrument blank and many of the samples were below the LLOQ (<4.96 pg/µL) it was deemed that the methanol blanks were contaminated, not the instrument. Based on this fact and that none of the samples were from tests specifically for (this run consisted of the 3rd transfer efficiency tests for PFOS and PFBS), the results for were accepted.

A blank PUF cartridge was extracted with each set of samples and analyzed. This analysis showed less than one half the area counts of the lower limit of quantitation for each analyte, thus meeting the acceptance criterion for blank sample results.

5.4 Laboratory Control Spikes

Laboratory Control Spikes (LCS) consisted of PUF cartridges spiked at known levels of 1 µg and 10 µg were prepared with each set of PUF samples. Each LCS was spiked by removing the large plastic endcap at the wide end of the cartridge and injecting the appropriate amount of spiking solution just below the surface of the PUF. The LCS was allowed to dry for at least 30 minutes before it was extracted as described in section 4 of the report.

The average PUF LCS recoveries for the 1 µg and 10 µg spikes are 82% and 92% respectively for PFOS, 80% and 90% respectively for PFBS, and 62% and 73% respectively for Sample results are not corrected for this recovery information. Summaries of each analysis of the LCSs are presented in Appendix B.

5.5 Sample Calculations

Sample Calculation:

$$\text{Final Result (ug)} = \text{Instrument Result (ug/L)} \times \text{Dilution Factor} \times \text{Extraction Volume (L)}$$

So for E02-0968-43362 (TE3-EX-PFOS-R-3)

$$\text{Final Result (ug)} = 270\frac{\text{ug}}{\text{L}} \times 50 \times 0.0102\ \text{L} = 138\ \text{ug}$$

Polyurethane Foam (PUF) Cartridge spike recoveries:

$$\text{Percent Recovery} = \frac{\text{Instrument Result (ug/L)} \times 0.02\ \text{L}}{\text{Spiked Amount (ug)}} \times 100$$

So for 020923LCS-1 (PFOS):

$$\text{Percent Recovery} = \frac{38.2\frac{\text{ug}}{\text{L}} \times 0.02\ \text{L}}{1.00\ \text{ug}} \times 100 = 76\%$$

6 Data Summary

Individual sample results are presented in appendix A. Each sample is identified with its respective LIMS number and the code that was associated with the sample upon arrival at 3M Environmental Laboratory. Sample results are given as pg/µL (or ng/mL or parts per billion) and in µg (if applicable) for each analyte of interest. Samples that were not detected above the lower limit of quantitation (LLOQ) are reported as less than quantities ("<") with the numerical value being the LLOQ for the analysis of that particular sample.

Laboratory Control Spikes are presented in appendix B and are reported in pg/µL and the percent recovery is given. Averages and standard deviations are only calculated for each spiking level of the Laboratory Control Spikes. Individual samples were not corrected for recovery.

7 Data / Sample Retention

The final report and raw data will be retained according to 3M Environmental Lab standard operating procedures.

8 Appendices

Appendix A: Individual Sample Results

Appendix B: Laboratory Control Spikes

Appendix C: Example Chromatograms

9 Signatures

12/12/02
Ph.D., Technical Manager Date

12/12/02
Quality Assurance Representative Date

12/12/02
Senior Research Chemist Date

Appendix A:
Individual Sample Results

Sample		PFOS* (pg/uL)	PFOS* (ug)	PFOS Corrected** (ug)	PFBS* (pg/uL)	PFBS* (ug)	PFBS Corrected** (ug)	(pg/uL)	(ug)	(ug)
E02-0820-42500	-600-1	<10.0	<0.20	<0.25	<10.1	<0.20	<0.23	<4.96	<0.099	<0.10
E02-0820-42502	900-1	<10.0	<0.20	<0.25	<10.1	<0.20	<0.23	<4.96	<0.099	<0.10
E02-0820-42504	-BLK-PUF	<10.0	<0.20	<0.25	<10.1	<0.20	<0.23	<4.96	<0.099	<0.10
E02-0820-42505	-1	14.9	0.082	0.10	<10.1	<0.056	<0.065	<4.96	<0.027	<0.028
E02-0820-42507	BLK	<10.0	<0.55	<0.68	<10.1	<0.056	<0.065	<4.96	<0.027	<0.028
E02-0821-42519	PFOS 1	232	1.3	1.6	<10.1	<0.056	<0.065	<4.96	<0.027	<0.028
E02-0821-42520	PFOS 2	40.5	0.22	0.28	<10.1	<0.056	<0.065	<4.96	<0.027	<0.028
E02-0821-42521	PFBS 1	14.7	0.081	0.10	146	0.80	0.93	<4.96	<0.027	<0.028
E02-0821-42522	PFBS 2	<10.0	<0.55	<0.68	10.2	0.056	0.065	<4.96	<0.027	<0.028
E02-0821-42523	PFS-BLK	<10.0	<0.55	<0.68	<10.1	<0.056	<0.065	<4.96	<0.027	<0.028
E02-0822-42526	-600-1	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0822-42527	-600-2	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0822-42528	-900-1	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0822-42529	-900-2	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0822-42530	K-PUF	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0822-42531	-1	<5.00	<0.028	<0.035	<5.05	<0.028	<0.032	<4.96	<0.027	<0.028
E02-0822-42532	-2	<5.00	<0.028	<0.035	<5.05	<0.028	<0.032	<4.96	<0.027	<0.028
E02-0822-42533	LK LIQ	<5.00	<0.028	<0.035	<5.05	<0.028	<0.032	<4.96	<0.027	<0.028
E02-0839-42697	-600-1	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0839-42698	-600-2	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0839-42699	900-1	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0839-42700	900-2	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0839-42701	LK-PUF	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0839-42702	-1	<5.00	<0.028	<0.035	<5.05	<0.028	<0.032	<4.96	<0.027	<0.028
E02-0839-42703	-2	<5.00	<0.028	<0.035	<5.05	<0.028	<0.032	<4.96	<0.027	<0.028
E02-0839-42704	BLK	<5.00	<0.028	<0.035	<5.05	<0.028	<0.032	<4.96	<0.027	<0.028
E02-0840-42708	FC1395-600-1	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0840-42709	FC1395-600-2	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0840-42710	FC1395-900-1	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0840-42711	FC1395-900-2	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0840-42712	FC1395-BLK-PUF	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0840-A	FC1395 EXTRACT	<5.00	<0.028	<0.035	<5.05	<0.028	<0.032	<4.96	<0.027	<0.028
E02-0840-B	FC1395 EXTRACT	<5.00	<0.028	<0.035	<5.05	<0.028	<0.032	<4.96	<0.027	<0.028
E02-0840-C	FC1395 EXTRACT	<5.00	<0.028	<0.035	<5.05	<0.028	<0.032	<4.96	<0.027	<0.028
E02-0867-42903	FC807-600-1	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0867-42904	FC807-600-2	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0867-42905	FC807-69BLK	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0867-42906	FC807-900-1	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0867-42907	FC807-900-2	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0867-42908	FC807-BLK-PUF	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0867-42909	FC807-0	<5.00	<0.014	<0.017	<5.05	<0.014	<0.016	<4.96	<0.014	<0.014
E02-0867-42910	FC807-1	<5.00	<0.028	<0.035	<5.05	<0.028	<0.032	<4.96	<0.027	<0.028
E02-0867-42911	FC807-2	<5.00	<0.028	<0.035	<5.05	<0.028	<0.032	<4.96	<0.027	<0.028
E02-0867-42912	FC807-BLK	<5.00	<0.028	<0.035	<5.05	<0.028	<0.032	<4.96	<0.027	<0.028
E02-0895-42970	PFOS-600-1	25.1	0.50	0.62	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0895-42971	PFOS-600-2	64.0	1.3	1.6	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0895-42972	PFOS-69BLK	6.32	0.13	0.16	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0895-42973	PFOS-900-1	4.31	0.086	0.11	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0895-42974	PFOS-900-2	9.01	0.18	0.22	25.8	0.52	0.60	<4.96	<0.099	<0.10
E02-0895-42975	PFOS-BLK-PUF	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0895-42976	PFOS-0	25.5	0.070	0.09	17.0	0.047	0.054	<4.96	<0.014	<0.014
E02-0895-42977	PFOS-1	15.4	0.085	0.11	7.11	0.039	0.045	<4.96	<0.027	<0.028
E02-0895-42978	PFOS-2	8.61	0.047	0.059	<5.05	<0.028	<0.032	<4.96	<0.027	<0.028
E02-0895-42979	PFOS-BLK	6.06	0.033	0.041	<5.05	<0.028	<0.032	<4.96	<0.027	<0.028
E02-0896-42983	PFBS-600-1	<5.00	<0.10	<0.12	84.5	1.7	2.0	<4.96	<0.099	<0.10
E02-0896-42984	PFBS-600-2	<5.00	<0.10	<0.12	85.6	1.7	2.0	<4.96	<0.099	<0.10
E02-0896-42985	PFBS-69BLK	<5.00	<0.10	<0.12	19.3	0.39	0.45	26.2	0.52	0.54
E02-0896-42986	PFBS-900-1	<5.00	<0.10	<0.12	320	6.4	7.4	<4.96	<0.099	<0.10
E02-0896-42987	PFBS-900-2	<5.00	<0.10	<0.12	9.63	0.19	0.22	<4.96	<0.099	<0.10
E02-0896-42988	PFBS-BLK-PUF	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0896-42989	PFBS-1	<5.00	<0.028	<0.035	169	0.93	1.1	15.4	0.085	0.087
E02-0896-42990	PFBS-2	<5.00	<0.028	<0.035	60.3	0.33	0.39	<4.96	<0.027	<0.028

Sample		PFOS* (pg/uL)	PFOS* (ug)	PFOS Corrected** (ug)	PFBS* (pg/uL)	PFBS* (ug)	PFBS Corrected** (ug)	(pg/uL)	(ug)	(ug)
E02-0896-42991	PFBS-BLK	<5.00	<0.028	<0.035	35.4	0.19	0.23	<4.96	<0.027	<0.028
E02-0898-42995	-600-1	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0898-42996	-600-2	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0898-42997	69BLK	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0898-42998	-900-1	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0898-42999	-900-2	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0898-43000	LK-PUF	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0898-43001	-1	<5.00	<0.028	<0.035	<5.05	<0.028	<0.032	<4.96	<0.027	<0.028
E02-0898-43002	-2	<5.00	<0.028	<0.035	<5.05	<0.028	<0.032	<4.96	<0.027	<0.028
E02-0898-43003	-BLK	<5.00	<0.028	<0.035	<5.05	<0.028	<0.032	<4.96	<0.027	<0.028
E02-0899-43007	HB2-600-1	<10.0	<0.20	<0.25	<10.1	<0.20	<0.23	<4.96	<0.099	<0.10
E02-0899-43009	HB2-900-1	<10.0	<0.20	<0.25	<10.1	<0.20	<0.23	<4.96	<0.099	<0.10
E02-0899-43011	HB2-BLK-PUF	<10.0	<0.20	<0.25	<10.1	<0.20	<0.23	<4.96	<0.099	<0.10
E02-0916-43081	TE-1	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0916-43082	TE-2	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0916-43083	PFBS-TE-1	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0916-43084	PFBS-TE-2	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0916-43085	PFOS-TE-1	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0916-43086	PFOS-TE-2	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0916-43087	TE-BLK	<5.00	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0917-43090	TE2-1	<10.0	<0.20	<0.25	<25.2	<0.20	<0.23	<4.96	<0.099	<0.10
E02-0917-43091	TE2-2	<10.0	<0.20	<0.25	11.2	0.22	0.26	<4.96	<0.099	<0.10
E02-0917-43092	PFBS-TE2-1	119	2.4	3.0	<25.2	<0.20	<0.23	<4.96	<0.099	<0.10
E02-0917-43093	PFBS-TE2-2	<10.0	<0.20	<0.25	<10.1	<0.20	<0.23	<4.96	<0.099	<0.10
E02-0917-43094	PFOS-TE2-1	<10.0	<0.20	<0.25	<25.2	<0.20	<0.23	<4.96	<0.099	<0.10
E02-0917-43095	PFOS-TE2-2	<10.0	<0.20	<0.25	<10.1	<0.20	<0.23	<4.96	<0.099	<0.10
E02-0917-43096	TE2-BLK	<10.0	<0.20	<0.25	<10.1	<0.20	<0.23	<4.96	<0.099	<0.10
E02-0917-43100	-TE2X-1	35.0	0.66	0.82	<25.2	<0.48	<0.56	6.89	0.13	0.13
E02-0917-43101	TE2X-2	<10.0	<0.19	<0.24	<10.1	<0.19	<0.22	<4.96	<0.094	<0.097
E02-0917-43102	-TE2X-BLK	<10.0	<0.19	<0.24	<10.1	<0.19	<0.22	<4.96	<0.094	<0.097
E02-0917-43103	PFBS-TE2X-1	233	4.4	5.5	805	15	18	<12.4	<0.24	<0.25
E02-0917-43104	PFBS-TE2X-2	<10.0	<0.19	<0.24	<10.1	<0.19	<0.22	<4.96	<0.094	<0.097
E02-0917-43105	PFBS-TE2X-BLK	<10.0	<0.19	<0.24	<10.1	<0.19	<0.22	<4.96	<0.094	<0.097
E02-0917-43106	PFOS-TE2X-1	897	17	21	<63.0	<1.20	<1.39	<12.4	<0.24	<0.25
E02-0917-43107	PFOS-TE2X-2	<10.0	<0.19	<0.24	<10.1	<0.19	<0.22	<4.96	<0.094	<0.097
E02-0917-43108	PFOS-TE2X-BLK	<10.0	<0.19	<0.24	<10.1	<0.19	<0.22	<4.96	<0.094	<0.097
E02-0926-43141	NHB-1	<5.00	<0.028	<0.035	<5.05	<0.028	<0.032	<4.96	<0.027	<0.028
E02-0926-43142	NHB-2	<5.00	<0.028	<0.035	<5.05	<0.028	<0.032	<4.96	<0.027	<0.028
E02-0926-43143	NHB-BLK	<5.00	<0.028	<0.035	<5.05	<0.028	<0.032	<4.96	<0.027	<0.028
E02-0968-43360	PFOS-HE-TE3-1	2330	47	58	37.4	0.75	0.87	<4.96	<0.099	<0.10
E02-0968-43361	PFOS-HE-TE3-2	44.0	0.88	1.1	<5.05	<0.10	<0.12	<4.96	<0.099	<0.10
E02-0968-43362	TE3-EX-PFOS-R-3	13530	138	171	237	2.4	2.8	<4.96	<0.050	<0.052
E02-0968-43363	TE3-EX-PFOS-R-4	150	1.5	1.9	<5.05	<0.052	<0.060	<4.96	<0.050	<0.052
E02-0968-43364	TE3-EX-PFOS-V-3	2218	6.2	7.7	47.4	0.13	0.15	<4.96	<0.014	<0.014
E02-0968-43365	TE3-EX-PFOS-V-4	102	0.29	0.35	<5.05	<0.014	<0.016	<4.96	<0.014	<0.014
E02-0968-43366	TE3-EX-BLK-2	<10.0	***	***	<5.05	***	***	<4.96	***	***
E02-0968-43370	PFOS-BLK-TE3	<10.0	<0.20	<0.25	<5.05	<0.10	<0.12	<4.96	<0.99	<1.0
E02-0969-43371	PFOS-AIR-TE3-1	997	20	25	14.7	0.29	0.34	<4.96	<0.99	<1.0
E02-0969-43372	PFOS-AIR-TE3-2	<10.0	<0.10	<0.12	<5.05	<0.10	<0.12	<4.96	<0.99	<1.0
E02-0969-43373	TE3-EX-PFOS-R-1	1908	19	24	81.4	0.83	0.96	<4.96	<0.50	<0.52
E02-0969-43374	TE3-EX-PFOS-R-2	35.4	0.36	0.45	5.79	0.059	0.069	<4.96	<0.50	<0.52
E02-0969-43375	TE3-EX-PFOS-V-1	696	1.9	2.4	52.0	0.15	0.17	<4.96	<0.014	<0.014
E02-0969-43376	TE-EX-PFOS-V-2	22.8	0.064	0.079	<5.05	<0.014	<0.016	<4.96	<0.014	<0.014
E02-0970-43377	PFBS-AIR-TE3-1	<10.0	<0.20	<0.25	1255	25	29	<4.96	<0.99	<1.0
E02-0970-43378	PFBS-AIR-TE3-2	<10.0	<0.20	<0.25	15.8	0.32	0.37	<4.96	<0.99	<1.0
E02-0970-43379	TE3-EX-R-1	<10.0	<0.10	<0.12	883	9.0	10	<4.96	<0.050	<0.052
E02-0970-43380	TE3-EX-R-2	<10.0	<0.10	<0.12	12.8	0.13	0.15	<4.96	<0.050	<0.052
E02-0970-43381	TE3-EX-V-1	<10.0	<0.028	<0.035	3824	11	12	8.17	0.023	0.024
E02-0970-43382	TE3-EX-V-2	<10.0	<0.028	<0.035	69.9	0.20	0.23	<4.96	<0.014	<0.014
E02-0970-43383	PFBS-HE-TE3-1	<10.0	<0.20	<0.25	511	10	12	<4.96	<0.99	<1.0
E02-0970-43384	PFBS-HE-TE3-2	<10.0	<0.20	<0.25	<5.05	<0.10	<0.12	<4.96	<0.99	<1.0
E02-0970-43385	TE3-EX-R-3	<10.0	<0.10	<0.12	10484	107	124	<4.96	<0.050	<0.052

Sample		PFOS* (pg/uL)	PFOS* (ug)	PFOS Corrected** (ug)	PFBS* (pg/uL)	PFBS* (ug)	PFBS Corrected** (ug)	(pg/uL)	(ug)	(ug)
E02-0970-43386	TE3-EX-R-4	<10.0	<0.10	<0.12	420	4.3	5.0	11.9	0.12	0.12
E02-0971-43387	TE3-EX-V-3	<10.0	<0.028	<0.035	2510	7.0	8.2	<4.96	<0.014	<0.014
E02-0971-43388	TE3-EX-V-4	<10.0	<0.028	<0.035	71.6	0.20	0.23	<4.96	<0.014	<0.014
E02-0971-43392	PFBS-BLK-TE3	<10.0	<0.20	<0.25	<5.05	<0.10	<0.12	<4.96	<0.99	<1.0
E02-0971-43393	TE3-EX-BLK-1	<10.0	***	***	<5.05	***	***	<4.96	***	***

* PFOS and PFBS results are presented as corrected for purity as the anion. is corrected for purity and presented as the

** PFOS, PFBS and are presented uncorrected for purity and as the Corrections used as follows: PFOS: 0.8060 (0.869 purity x 0.9275 correction for potassium. PFBS: 0.8607 (0.973 purity x 0.8846 correction for potassium.)

*** These samples are just blanks of the methanol used in the study. There is no associated volume to calculate ug for these samples.

Appendix B:
Laboratory Control Spikes

Table 1: 1 ug Laboratory Control Spikes

Sample	PFOS (pg/uL)	percent recovery	RPD	PFBS (pg/uL)	percent recovery	RPD	(pg/uL)	percent recovery	RPD
020913LCS-1	43.4	87%	4.9%	43.5	86%	5.0%	34.5	69%	4.4%
020913LCS-2	45.6	91%		45.7	91%		36.0	73%	
020913LCS-1	45.6	91%	4.0%	43.9	87%	3.4%	35.4	71%	2.5%
020913LCS-2	47.4	95%		45.4	90%		36.3	73%	
020923LCS-1	38.2	76%	14%	35.4	70%	16%	25.5	51%	20%
020923LCS-2	44.0	88%		41.7	83%		31.1	63%	
020923LCS-1	37.1	74%	19%	38.1	75%	15%	26.8	54%	21%
020923LCS-2	44.8	90%		44.4	88%		33.0	66%	
020930LCS-1	35.3	71%	3.3%	35.6	71%	2.9%	25.5	51%	1.2%
020930LCS-2	36.5	73%		36.7	73%		25.8	52%	
021001LCS-1	34.7	69%	10%	34.6	68%	11%	24.6	50%	9.5%
021001LCS-2	38.4	77%		38.4	76%		27.1	55%	
020927LCS-1	41.5	83%	2.0%	39.7	79%	9.7%	32.3	65%	9.4%
020927LCS-2	42.3	85%		43.7	87%		35.5	72%	
Average	41.0	82%		40.5	80%		30.7	62%	
Standard Deviation	4.27	8.5%		4.02	8.0%		4.55	9.2%	
RSD	10%			10%			15%		

True values of the LCS samples are: PFOS 50.0 pg/uL (1.00 ug), PFBS 50.5 pg/uL (1.01 ug),
and
RPD=Relative Percent Difference

Table 2: 10 ug Laboratory Control Spikes

Sample	PFOS (pg/uL)	percent recovery	RPD	PFBS (pg/uL)	percent recovery	RPD	(pg/uL)	percent recovery	RPD
020913LCS-3	464	93%	6.8%	450	89%	9.3%	357	72%	14.1%
020913LCS-4	497	99%		495	98%		411	83%	
020913LCS-3	489	98%	5.9%	473	94%	7.0%	372	75%	13.1%
020913LCS-4	519	104%		507	100%		424	86%	
020923LCS-3	414	83%	4.6%	*	*		320	65%	6.8%
020923LCS-4	433	87%		*	*		343	69%	
020923LCS-3	434	87%	4.3%	405	80%	3.9%	331	67%	6.3%
020923LCS-4	453	91%		421	83%		353	71%	
020923LCS-3	425	85%	4.6%	*	*		337	68%	8.1%
020923LCS-4	445	89%		*	*		365	74%	
020923LCS-3	458	92%	3.7%	437	87%	4.8%	352	71%	6.5%
020923LCS-4	476	95%		459	91%		376	76%	
Average	459	92%		456	90%		362	73%	
Standard Deviation	31.6	6.3%		34.9	6.9%		31.0	6.3%	
RSD	7%			8%			9%		

True values of the LCS samples are: PFOS 500 pg/uL (10.0 ug), PFBS 505 pg/uL (10.1 ug),
and

* Values were above the upper limit of quantitation for that analysis (nominal concentration of 250 pg/uL). For that analysis the high calibration point (nominal concentration of 500 pg/uL) was excluded in order to quantitate samples at a lower LLOQ (lower limit of quantitation). In other words, the 500 pg/uL standard was excluded to make the lowest standard within the +/- 30% criteria. These spikes were run again at a later date and all results for all analytes are presented here.

Appendix C:
Example Chromatograms

Data File: \\Etstarget\target\chem\itchy.i\I021004.b\ITCHY022.D Page 1
Report Date: 14-Oct-2002 09:16

3M Environmental Laboratory

Data file : \\Etstarget\target\chem\itchy.i\I021004.b\ITCHY022.D
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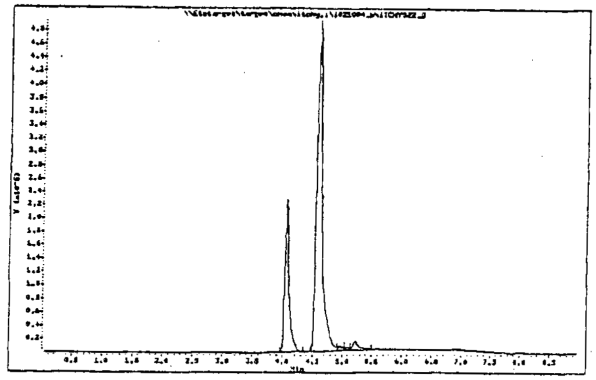
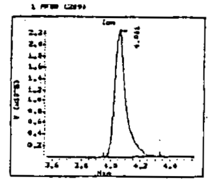
Inj Date : 04-OCT-2002 14:40
Operator : Inst ID: itchy.i
Smp Info : 4 calibration standard
Misc Info :
Comment :
Method : \\Etstarget\target\chem\itchy.i\I021004.b\I021004.m
Meth Date : 14-Oct-2002 09:16 eich Quant Type: ESTD
Cal Date : 04-OCT-2002 14:40 Cal File: ITCHY022.D
Als bottle: 4 Calibration Sample, Level: 4
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

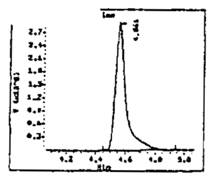
Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	AMOUNTS CAL-AMT (ng/ml)	ON-COL (ng/ml)
1 PFBS (299)	299	4.060	4.060	0.000	1190075	50.3000	50.2
2 L16271 (366)	500	4.560	4.560	0.000	1650925	48.4000	48.7
3 PFOS (499)	499	4.600	4.600	0.300	1912017	50.0000	49.1

Data File: \\Etstarget\target\chem\itchy.i\I021004.b\ITCHY022.D Page 2



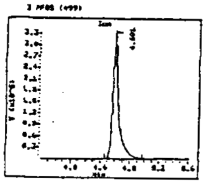
1 PFBS (299)





Data File: \\Etstarget\target\chem\itchy.i\I021004.b\ITCHY022.D Page 3

3 PFOS (499)



Data File: \\Etstarget\target\chem\itchy.i\I020926.b\ITCHY053.D Page 1
Report Date: 14-Oct-2002 10:00

3M Environmental Laboratory

Data file : \\Etstarget\target\chem\itchy.i\I020926.b\ITCHY053.D
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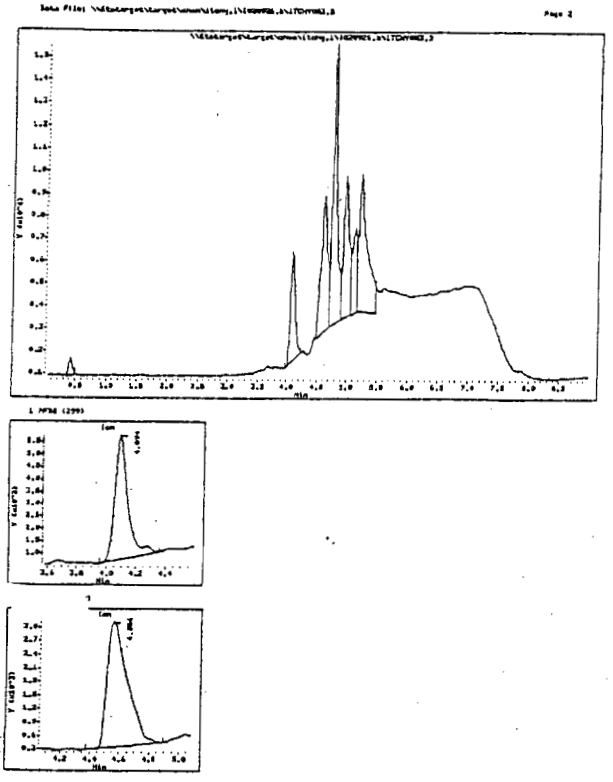
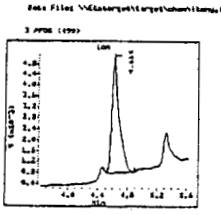
Inj Date : 27-SEP-2002 00:01
Operator : kje Inst ID: itchy.i
Smp Info : TN-A-4520
Misc Info :
Comment :
Method : \\Etstarget\target\chem\itchy.i\I020926.b\I020926.m
Meth Date : 09-Oct-2002 09:22 eich Quant Type: ESTD
Cal Date : 26-SEP-2002 18:45 Cal File: ITCHY023.D
Als bottle: 91
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/ml)	FINAL (ng/ml)
1 PFBS (299)	299	4.095	4.083	0.010	30172	1671.61	1670(M)
2 L16271 (366)	500	4.563	4.573	-0.020	26034	6700.71	6700(M)
3 PFOS (499)	499	4.513	4.523	-0.010	30206	3154.47	3160(M)

QC Flag Legend

M - Compound response manually integrated.





Data File: \\Etstarget\target\chem\itchy.i\I020926.b\ITCHY039.D Page 1
Report Date: 14-Oct-2002 10:00

3M Environmental Laboratory

Data File : \\Etstarget\target\chem\itchy.i\I020926.b\ITCHY039.D
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Operator : kje Inst ID: itchy.i
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Misc Info :
Comment :
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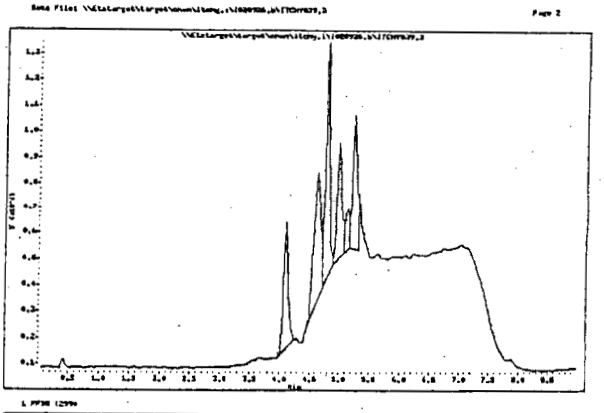
Meth Date : 09-Oct-2002 09:22 eich Quant Type: ESTD
Cal Date : 26-SEP-2002 18:45 Cal File: ITCHY023.D
Als bottle: 92
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

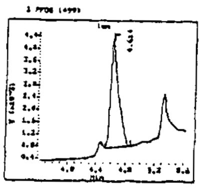
Compounds	Quant Ion Mass	RT	Resp RT	Dlta RT	Response	Concentrations On-Column (ng/mL)	Final (ng/mL)
1 PFBS (299)	299	4.096	1.001	0.011	38968	1671.89	1670(M)
2 L462371 (540)	896	4.584	0.973	-0.010	29471	2700.16	2700(M)
3 PFBS (299)	499	4.614	0.627	-0.009	27661	3160.76	3160(M)

QC Flag Legend

M - Compound response manually integrated.



Data File: [illegible] Page 3



Data File: \\Etstarget\target\chem\itchy.i\I021004.b\ITCHY032.D Page 1
Report Date: 14-Oct-2002 09:21

3M Environmental Laboratory

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Operator :
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Smp Info : 0
Misc Info :
Comment :
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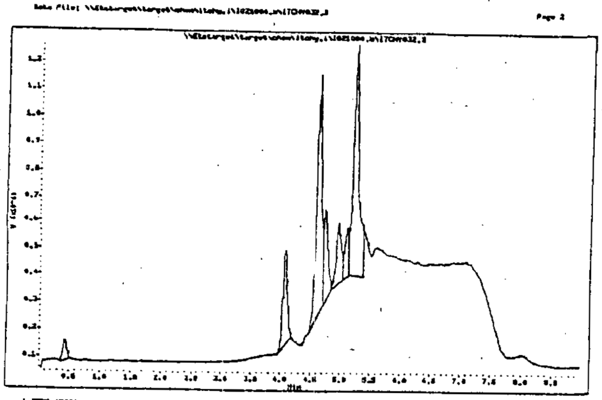
Meth Date : 14-Oct-2002 09:16 eich
Quant Type: ESTD
Cal Date : 04-OCT-2002 14:40
Cal File: ITCHY022.D
Als bottle: 93
Dil Factor: 1.00000
Integrator: Falcon
Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

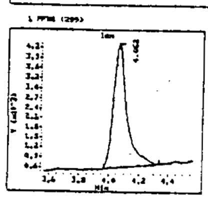
Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/mL)	FINAL (ng/mL)
1 PFBS (299)	299	4.361	4.360	0.001	31333	1119.46	1160(M)
2 L16291 (540)	540	4.541	4.558	-0.013	3013	0.86981	0.8650(M)
3 PFOS (499)	499	4.612	4.600	0.011	65978	1135.84	1140(M)

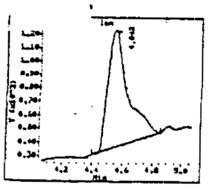
QC Flag Legend

M - Compound response manually integrated.

Data File: \\Etstarget\target\chem\itchy.i\I021004.b\ITCHY032.D Page 2







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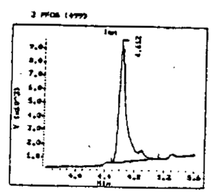

Data File: \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY028.D Page 1
Report Date: 14-Oct-2002 09:53

3M Environmental Laboratory

Data file : \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY028.D
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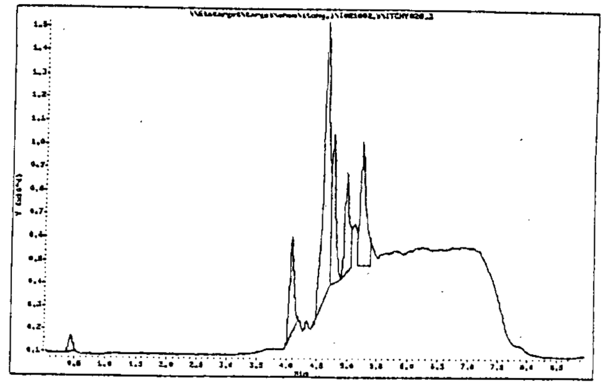
Inj Date : 02-OCT-2002 20:29
Operator : kje Inst ID: itchy.i
Smp Info : PFBS-BLK-PUF
Misc Info :
Comment :
Method : \\Etstarget\target\chem\itchy.i\I021002.b\I021002.m
Meth Date : 14-Oct-2002 09:53 eich Quant Type: ESTD
Cal Date : 02-OCT-2002 19:47 Cal File: ITCHY024.D
Als bottle: 21
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

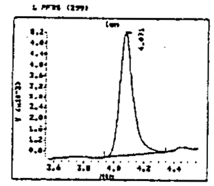
Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/mL)	FINAL (ng/mL)
1 PFBS (299)	299	4.078	4.061	0.009	35653	1230.14	1310(M)
2 [illegible] (538)	500	4.510	4.561	-0.031	30994	0.11608	0.116(M)
3 PFOS (499)	499	4.630	4.611	0.009	61734	1281.46	1280(M)

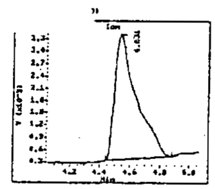
QC Flag Legend

M - Compound response manually integrated.

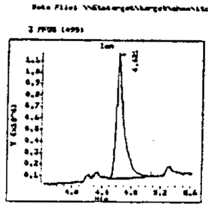
Data File: \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY028.D Page 2







Data File: \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY028.D Page 3



Data File: \\Etstarget\target\chem\itchy.i\I021004.b\ITCHY047.D Page 1
Report Date: 14-Oct-2002 09:22

3M Environmental Laboratory

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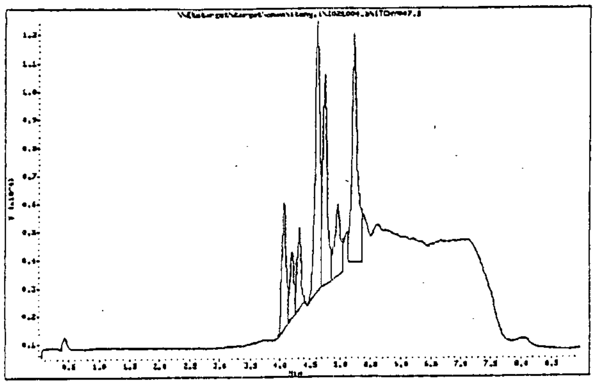
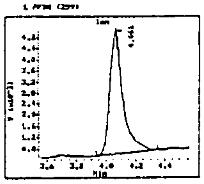
Inj Date : 04-OCT-2002 18:57
Operator : Inst ID: itchy.i
Smp Info :
Misc Info :
Comment :
Method : \\Etstarget\target\chem\itchy.i\I021004.b\I021004.m
Meth Date : 14-Oct-2002 09:16 eich Quant Type: ESTD
Cal Date : 04-OCT-2002 14:40 Cal File: ITCHY022.D
Als bottle: 54
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

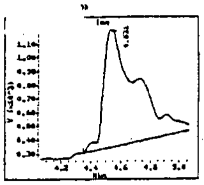
Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/mL)	FINAL (ng/mL)
1 PFBS (299)	299	4.061	4.060	0.001	77616	1119.50	1140(M)
2 [illegible] (380)	380	4.531	4.560	-0.029	14992	0.29991	0.299(M)
3 PFOS (499)	499	4.611	4.600	0.011	71684	1133.70	1140(M)

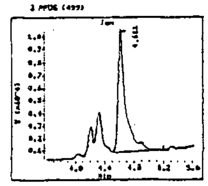
QC Flag Legend

M - Compound response manually integrated.









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Report Date: 14-Oct-2002 09:22

                    3M Environmental Laboratory

Data file : \\Etstarget\target\chem\itchy.i\I021004.b\ITCHY057.D
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Operator  :                              Inst ID: itchy.i
Smp Info  :
Misc Info :
Comment   :
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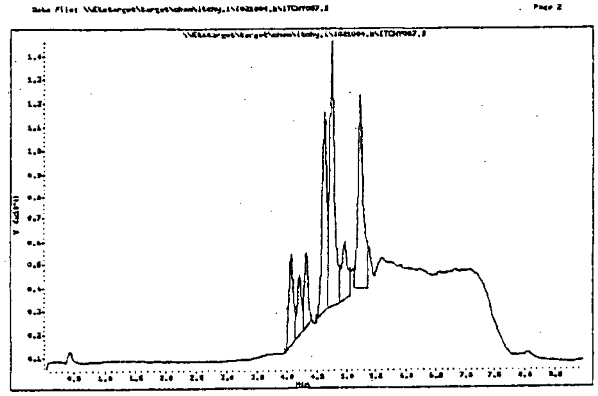
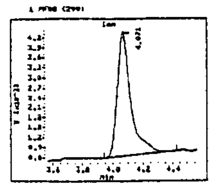
Meth Date : 14-Oct-2002 09:16 eich       Quant Type: ESTD
Cal Date  : 04-OCT-2002 14:40            Cal File: ITCHY022.D
Als bottle: 61
Dil Factor: 1.00000
Integrator: Falcon                       Compound Sublist: all.sub
Target Version:  4.10
Processing Host: W19559
```

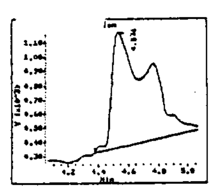
Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/mL)	FINAL (ng/mL)
1 [illegible] (399)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible](M)
2 [illegible] (500)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible](M)
3 [illegible] (499)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible](M)

QC Flag Legend

M - Compound response manually integrated.

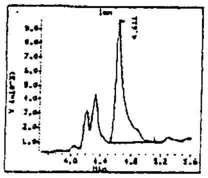






Page 3

3 PFOS (499)



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Report Date: 14-Oct-2002 10:29

3M Environmental Laboratory

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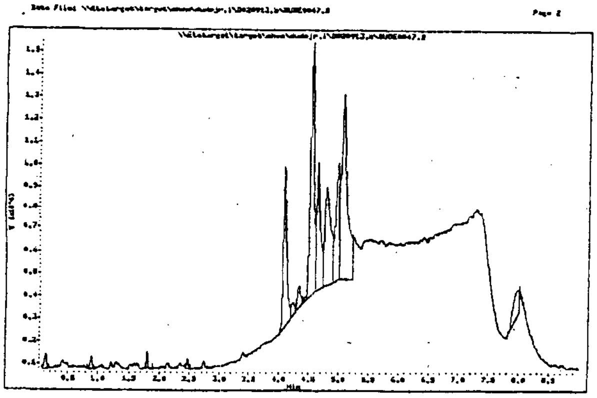
Misc Info :
Comment :
Method : \\Etstarget\target\chem\dudejr.i\D020913.b\D020913.m
Meth Date : 08-Oct-2002 13:26 eich Quant Type: ESTD
Cal Date : 13-SEP-2002 19:20 Cal File: DUDE0025.D
Als bottle: 32
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

Compounds	QUANT SIG MASS	RT	EXP RT	REL RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/mL)	FINAL (ng/mL)
1 PFBS (299)	299	4.004	4.074	0.004	27145	2448.12	2450
2 [illegible] (504)	504	4.493	4.493	0.001	4204	7321.16	7320
3 PFOS (499)	499	4.526	4.527	0.001	44160	3247.13	3250(M)

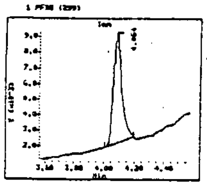
QC Flag Legend

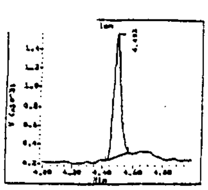
M - Compound response manually integrated.

Page 2



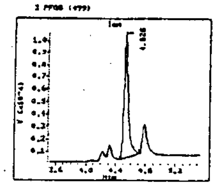
1 PFBS (299)





Page 3

3 PFOS (499)



Data File: \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY029.D Page 1
Report Date: 14-Oct-2002 09:28

3M Environmental Laboratory

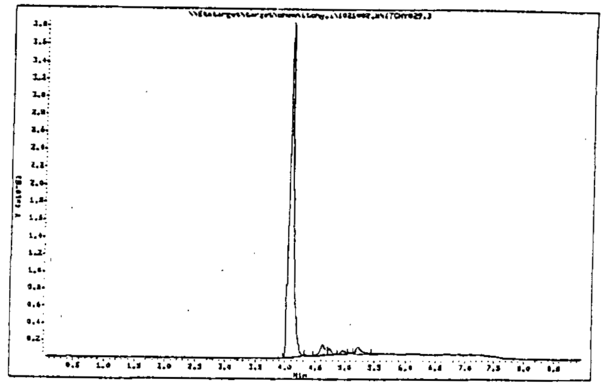
Data file : \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY029.D
Lab Smp Id: E02-0896-42984
Inj Date : 02-OCT-2002 20:39
Operator : kje Inst ID: itchy.i
Smp Info : PFBS-600-2
Misc Info :
Comment :
Method : \\Etstarget\target\chem\itchy.i\I021002.b\I021002.m
Meth Date : 09-Oct-2002 10:40 itchy.i Quant Type: ESTD
Cal Date : 02-OCT-2002 19:47 Cal File: ITCHY024.D
Als bottle: 22
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/mL)	FINAL (ng/mL)
1 PFBS (299)	299	4.061	4.061	0.000	[illegible]	[illegible]	[illegible]
2 [illegible] (500)	500	4.531	4.565	-0.034	[illegible]	[illegible]	[illegible](M)
3 PFOS (499)	499	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible](M)

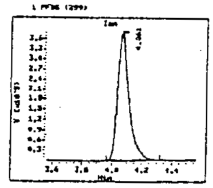
QC Flag Legend

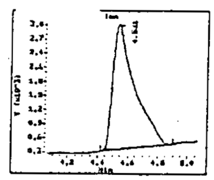
M - Compound response manually integrated.

Data File: \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY029.D Page 2



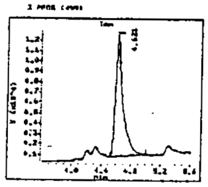
1 PFBS (299)





Data File: \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY029.D Page 3

3 PFOS (499)



Data File: \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY039.D Page 1
Report Date: 14-Oct-2002 09:28

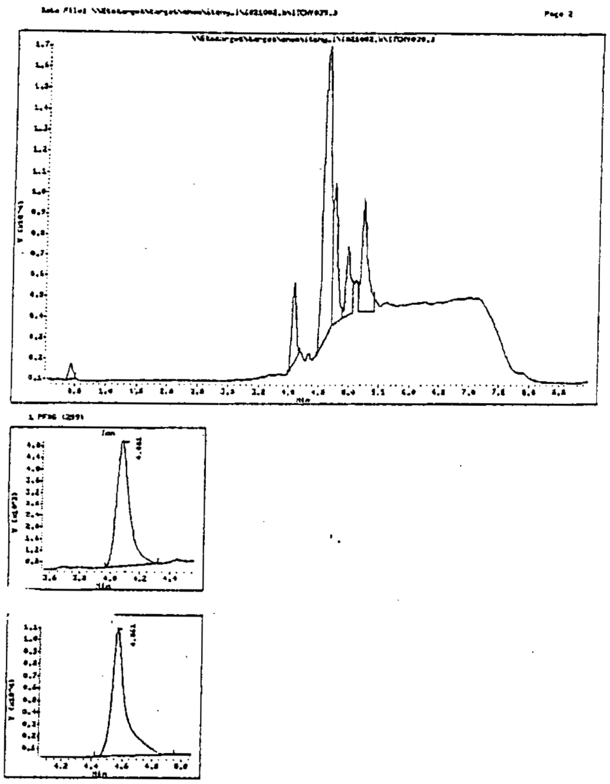
3M Environmental Laboratory

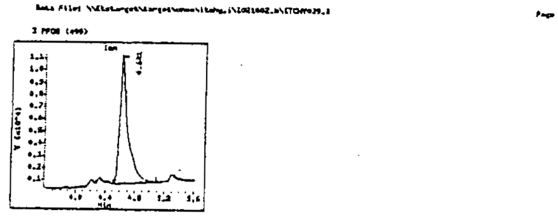
Data file : \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY039.D
Lab Smp Id: E02-0898-42996
Inj Date : 02-OCT-2002 22:24
Operator : kje Inst ID: itchy.i
Smp Info :
Misc Info :
Comment :
Method : \\Etstarget\target\chem\itchy.i\I021002.b\I021002.m
Meth Date : 09-Oct-2002 10:40 itchy.i Quant Type: ESTD
Cal Date : 02-OCT-2002 19:47 Cal File: ITCHY024.D
Als bottle: 28
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/mL)	FINAL (ng/mL)
1 PFBS (299)	299	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible](M)
2 [illegible] (500)	500	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible](M)
3 PFOS (499)	499	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible](M)

QC Flag Legend

M - Compound response manually integrated.





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Data File: \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY043.D   Page 1
Report Date: 14-Oct-2002 09:28

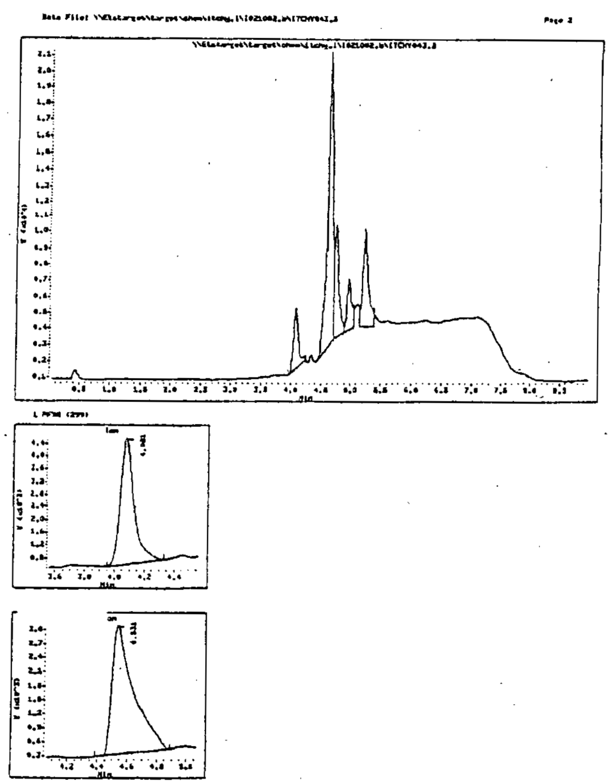
                       3M Environmental Laboratory

Data file : \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY043.D
Lab Smp Id: E02-0898-42999
Inj Date  : 02-OCT-2002 23:06
Operator  :                               Inst ID: itchy.i
Smp Info  :
Misc Info :
Comment   :
Method    : \\Etstarget\target\chem\itchy.i\I021002.b\I021002.m
Meth Date : 09-Oct-2002 10:40 itchy.i     Quant Type: ESTD
Cal Date  : 02-OCT-2002 19:47             Cal File: ITCHY024.D
Als bottle: 31
Dil Factor: 1.00000
Integrator: Falcon                        Compound Sublist: all.sub
Target Version:  4.10
Processing Host: W19559
```

Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/ml)	FINAL (ng/ml)
1 PFHS (299)	299	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
2 L18PFS (503)	503	[illegible]	4.561	-0.011	[illegible]	[illegible]	[illegible]
3 PFOS (499)	499	[illegible]	4.611	[illegible]	[illegible]	[illegible]	[illegible]

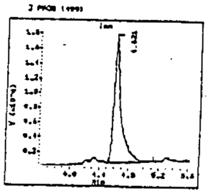
QC Flag Legend

M - Compound response manually integrated.



Data File: \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY050.D Page 3

3 PFOS (499)



Data File: \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY050.D Page 1
Report Date: 14-Oct-2002 09:28

3M Environmental Laboratory

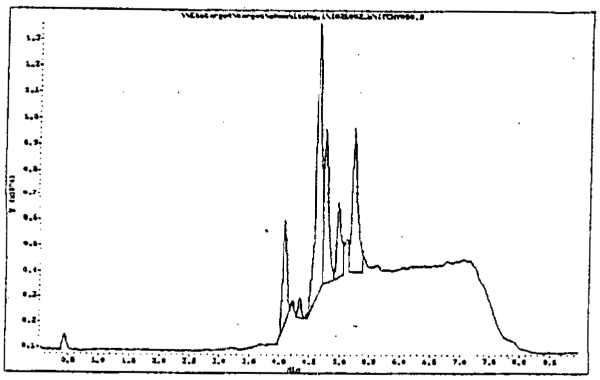
Data file : \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY050.D
Lab Smp Id: S02-0867-42903
Inj Date : 03-OCT-2002 00:20
Operator : kje Inst ID: itchy.i
Smp Info : FC807-600-1
Misc Info :
Comment :
Method : \\Etstarget\target\chem\itchy.i\I021002.b\I021002.m
Meth Date : 09-Oct-2002 10:40 itchy.i Quant Type: ESTD
Cal Date : 02-OCT-2002 19:47 Cal File: ITCHY024.D
Als bottle: 35
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/mL)	FINAL (ng/mL)
1 PFHS (299)	299	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible](M)
2 [illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible](M)
3 PFOS (499)	499	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible](M)

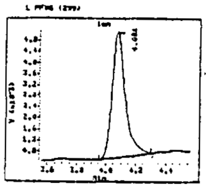
QC Flag Legend

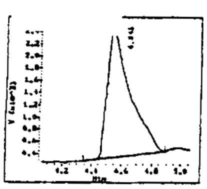
M - Compound response manually integrated.

Data File: \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY050.D Page 2



1 PFHS (299)





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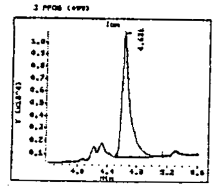
3 PFOS (499)



Data File: \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY062.D Page 1
Report Date: 14-Oct-2002 09:28

3M Environmental Laboratory

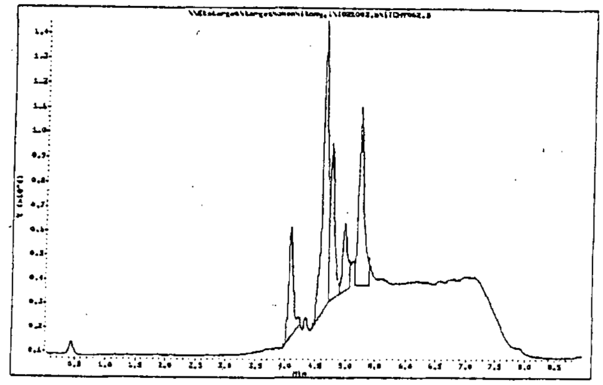
Data file : \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY062.D
Lab Smp Id: E02-0840-42711
Inj Date : 03-OCT-2002 02:27
Operator : kje Inst ID: itchy.i
Smp Info : FC1395-900-2
Misc Info :
Comment :
Method : \\Etstarget\target\chem\itchy.i\I021002.b\I021002.m
Meth Date : 09-Oct-2002 10:40 itchy.i Quant Type: ESTD
Cal Date : 02-OCT-2002 19:47 Cal File: ITCHY024.D
Als bottle: 42
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/mL)	FINAL (ng/mL)
1 PFHS (299)	299	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1230(M)
2 [illegible] (500)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	2200(M)
3 PFOS (499)	499	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1200(M)

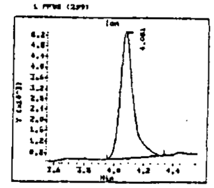
QC Flag Legend

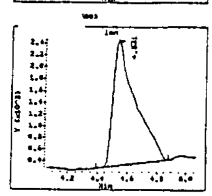
M - Compound response manually integrated.

Data File: \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY062.D Page 2



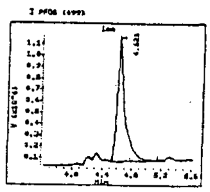
1 PFHS (299)





Data File: \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY062.D Page 3

3 PFOS (499)



Data File: \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY063.D Page 1
Report Date: 14-Oct-2002 09:28

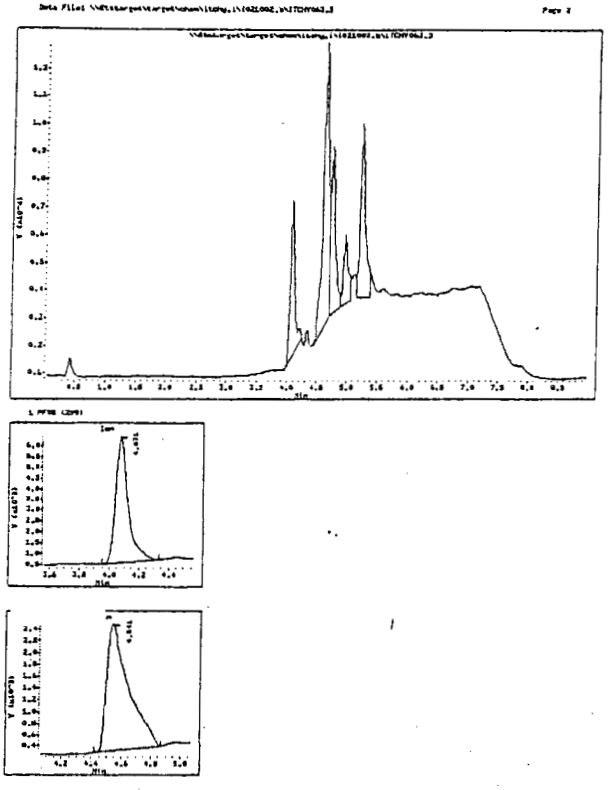
3M Environmental Laboratory

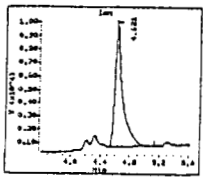
Data file : \\Etstarget\target\chem\itchy.i\I021002.b\ITCHY063.D
Lab Smp Id: E02-0840-42710
Inj Date : 03-OCT-2002 02:37
Operator : kje Inst ID: itchy.i
Smp Info : FC1395-900-1
Misc Info :
Comment :
Method : \\Etstarget\target\chem\itchy.i\I021002.b\I021002.m
Meth Date : 09-Oct-2002 10:40 itchy.i Quant Type: ESTD
Cal Date : 02-OCT-2002 19:47 Cal File: ITCHY024.D
Als bottle: 41
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/mL)	FINAL (ng/mL)
1 PFHS (299)	299	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1230(M)
2 [illegible] (500)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	2200(M)
3 PFOS (499)	499	4.620	4.611	[illegible]	[illegible]	[illegible]	1200(M)

QC Flag Legend

M - Compound response manually integrated.





Data File: \\Etstarget\target\chem\itchy.i\I021004.b\ITCHY039.D Page 1
Report Date: 14-Oct-2002 09:22

3M Environmental Laboratory

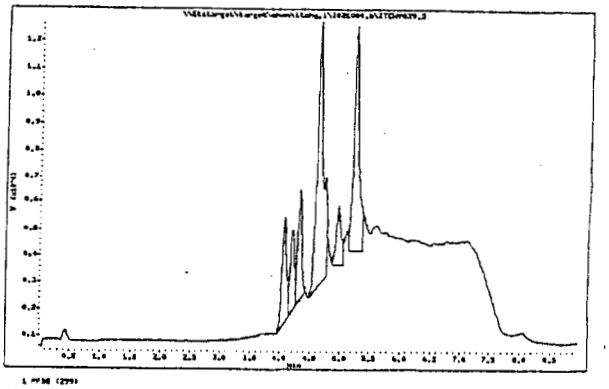
Data file : \\Etstarget\target\chem\itchy.i\I021004.b\ITCHY039.D
Lab Smp Id: E02-0839-42698
Inj Date : 04-OCT-2002 17:35
Operator :
Smp Info :
Misc Info :
Comment :
Method : \\Etstarget\target\chem\itchy.i\I021004.b\I021004.m
Meth Date : 14-Oct-2002 09:16 eich
Cal Date : 04-OCT-2002 14:40
Als bottle: 50
Dil Factor: 1.00000
Integrator: Falcon
Target Version: 4.10
Processing Host: W19559

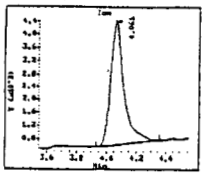
Inst ID: itchy.i
Quant Type: ESTD
Cal File: ITCHY022.D
Compound Sublist: all.sub

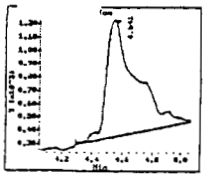
Compounds	Quant Ion Mass	RT	Exp RT	Dlta RT	Response	Conc (ng/mL)	Final (ng/mL)
1 PFOA (299)	299	4.064	4.000	0.065	23661	1128.63	1128(M)
2 13C4PFOA (304)	304	4.061	4.066	-0.005	12169	0.21267	0.213(M)
3 PFOS (499)	499	6.611	6.666	0.011	64956	1125.66	1126(M)

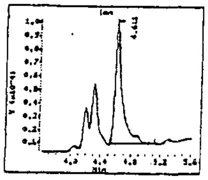
QC Flag Legend

M - Compound response manually integrated.









Data File: \\Etstarget\target\chem\dudejr.i\D020924.b\DUDE0030.D Page 1
Report Date: 14-Oct-2002 10:15

3M Environmental Laboratory

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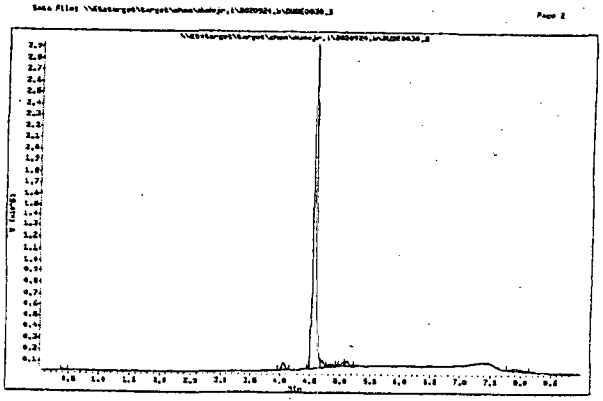
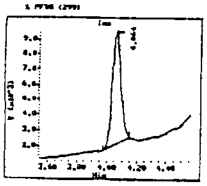
Data file  : \\Etstarget\target\chem\dudejr.i\D020924.b\DUDE0030.D
Lab Smp Id: E02-0968-43360
Inj Date   : 24-SEP-2002 18:58
Operator   : kje                              Inst ID: dudejr.i
Smp Info   : PFOS-KE-TE3-1 500F
Misc Info  :
Comment    :
Method     : \\Etstarget\target\chem\dudejr.i\D020924.b\D020924.m
Meth Date  : 09-Oct-2002 08:07 eich           Quant Type: ESTD
Cal Date   : 24-SEP-2002 17:55                Cal File: DUDE0024.D
Als bottle: 21
Dil Factor: 1.00000
Integrator: Falcon                            Compound Sublist: all.sub
Target Version:  4.10
Processing Host: W19559
```

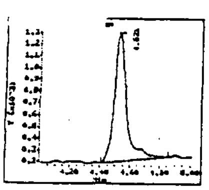
Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/mL)	FINAL (ng/mL)
1 PFBS (299)	299	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
2 L46271 (500)	500	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible](M)
3 PFOS (499)	499	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	499	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

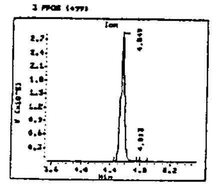
QC Flag Legend

M - Compound response manually integrated.









Data File: \\Etstarget\target\chem\dudejr.i\D020924.b\DUDE0032.D Page 1
Report Date: 14-Oct-2002 10:15

3M Environmental Laboratory

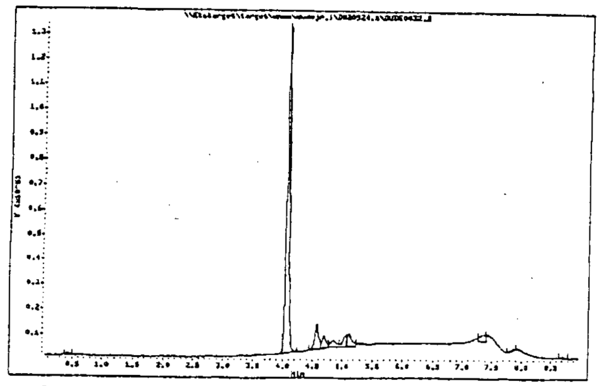
Data file : \\Etstarget\target\chem\dudejr.i\D020924.b\DUDE0032.D
Lab Smp Id: E02-0970-43377
Inj Date : 24-SEP-2002 19:19
Operator : kje Inst ID: dudejr.i
Smp Info : PFBS-AIR-TB1-1 500F
Misc Info :
Comment :
Method : \\Etstarget\target\chem\dudejr.i\D020924.b\D020924.m
Meth Date : 09-Oct-2002 08:07 eich Quant Type: ESTD
Cal Date : 24-SEP-2002 17:55 Cal File: DUDE0024.D
Als bottle: 23
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/mL)	FINAL (ng/mL)
1 PFBS (299)	299	[illegible]	[illegible]	0.000	[illegible]	[illegible]	[illegible]
2 [illegible] (366)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
3 PFOS (499)	499	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
	499	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

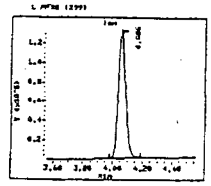
QC Flag Legend

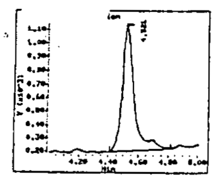
M - Compound response manually integrated.

Data File: \\Etstarget\target\chem\dudejr.i\D020924.b\DUDE0032.D Page 2



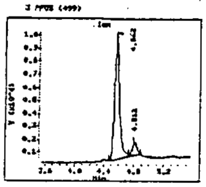
1 PFBS (299)





Data File: \\Etstarget\target\chem\dudejr.i\D020924.b\DUDE0032.D Page 3

3 PFOS (499)



Data File: \\Etstarget\target\chem\itchy.i\I020926.b\ITCHY027.D Page 1
Report Date: 14-Oct-2002 09:53

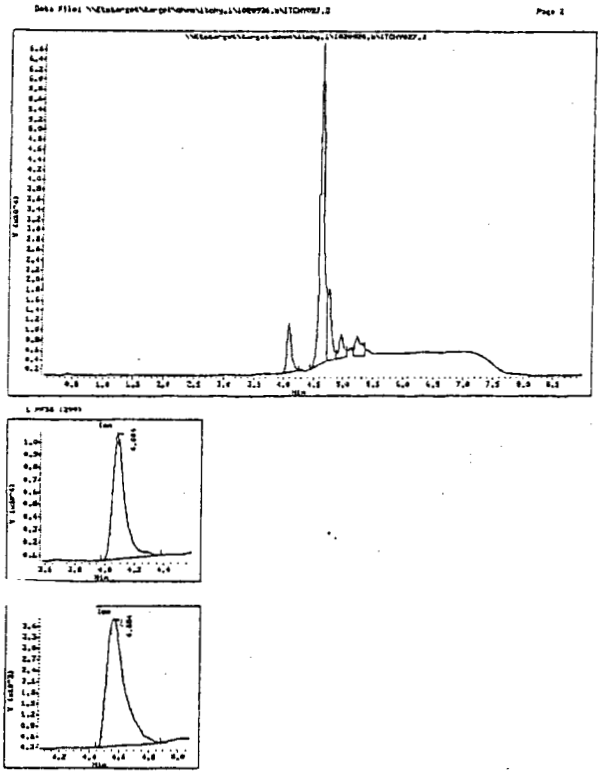
3M Environmental Laboratory

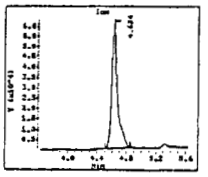
Data file : \\Etstarget\target\chem\itchy.i\I020926.b\ITCHY027.D
Lab Smp Id: E02-0895-42979
Inj Date : 26-SEP-2002 19:27
Operator : kje Inst ID: itchy.i
Smp Info : PFOS-BLK
Misc Info :
Comment :
Method : \\Etstarget\target\chem\itchy.i\I020926.b\I020926.m
Meth Date : 09-Oct-2002 09:22 eich Quant Type: ESTD
Cal Date : 26-SEP-2002 18:45 Cal File: ITCHY023.D
Als bottle: 21
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/mL)	FINAL (ng/mL)
1 PFBS (299)	299	[illegible]	[illegible]	0.000	[illegible]	1670.67	1670(M)
2 [illegible] (366)	[illegible]	[illegible]	[illegible]	-0.020	[illegible]	[illegible]	[illegible](M)
3 PFOS (499)	499	[illegible]	[illegible]	0.000	[illegible]	[illegible]	[illegible]

QC Flag Legend

M - Compound response manually integrated.





Data File: \\Etstarget\target\chem\itchy.i\I020926.b\ITCKY043.D Page 1
Report Date: 14-Oct-2002 10:00

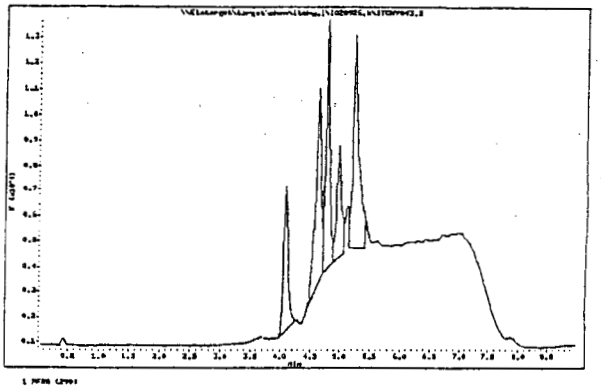
3M Environmental Laboratory

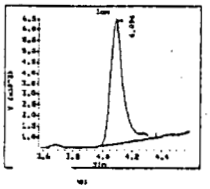
Data file : \\Etstarget\target\chem\itchy.i\I020926.b\ITCKY043.D
Lab Smp Id: E02-0822-425J3
Inj Date : 26-SEP-2002 22:16
Operator : Inst ID: itchy.i
Smp Info :
Misc Info :
Comment :
Method : \\Etstarget\target\chem\itchy.i\I020926.b\I020926.m
Meth Date : 09-Oct-2002 09:32 eich Quant Type: ESTD
Cal Date : 26-SEP-2002 18:45 Cal File: ITCHY023.D
Als bottle: 34
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

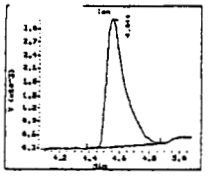
Compounds	(Quant Ion) Area	RT	Exp RT	Dev RT	Response	Concentrations On-Column (ng/mL)	Final (ng/mL)
1 PFOS (PFOS)	339	6.459	6.463	-0.011	36188	1871.45	1870282
2 C14371 (Std)	366	6.244	6.271	-0.039	39188	8780.98	8780195
3 PFOS (PFOS)	169	6.426	6.432	0.001	98864	3136.17	3136195

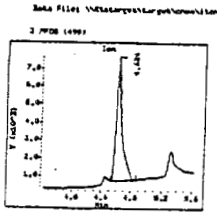
QC Flag Legend

M - Compound response manually integrated.









Data File: \\Etstarget\target\chem\itchy.i\I020926.b\ITCHY047.D Page 1
Report Date: 14-Oct-2002 10:00

3M Environmental Laboratory

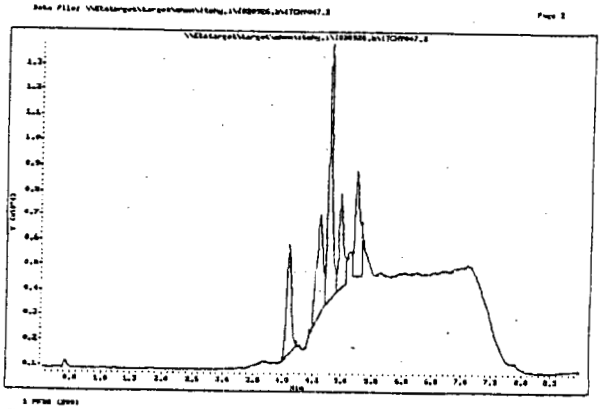
Data file : \\Etstarget\target\chem\itchy.i\I020926.b\ITCHY047.D
Lab Smp Id: E02-0867-42912
Inj Date : 26-SEP-2002 22:58
Operator : kje
Smp Info : FC807-BLK
Misc Info :
Comment :
Method : \\Etstarget\target\chem\itchy.i\I020926.b\I020926.m
Meth Date : 09-Oct-2002 09:32 eich
Cal Date : 26-SEP-2002 18:45
Als bottle: 37
Dil Factor: 1.00000
Integrator: Falcon
Target Version: 4.10
Processing Host: WI9559

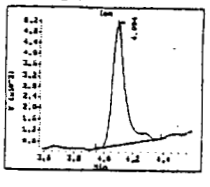
Inst ID: itchy.i
Quant Type: ESTD
Cal File: ITCHY021.D
Compound Sublist: all.sub

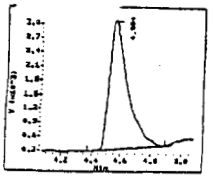
Compounds	QUANT ION MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/mL)	FINAL (ng/mL)
1 PFOS (SPS)	499	4.999	4.963	0.036	37806	1673.11	1674(M)
2 Li6371 (Sub)	399	4.363	4.373	-0.010	23466	8706.23	8708(M)
3 PFOS (APS)	499	4.812	4.823	-0.010	14435	1338.99	1340(M)

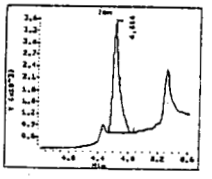
QC Flag Legend

M - Compound response manually integrated.









Data File: \\Etstarget\target\chem\dudejr.i\D020925A.b\DUDE0029.D Page 1
Report Date: 14-Oct-2002 10:27

3M Environmental Laboratory

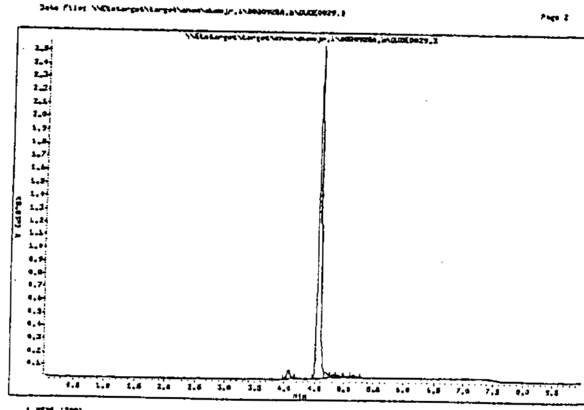
Data file : \\Etstarget\target\chem\dudejr.i\D020925A.b\DUDE0029.D
Lab Smp Id: E02-0968-43364
Inj Date : 25-SEP-2002 14:35
Operator : kje Inst ID: dudejr.i
Smp Info : TE3-EX-PFOS-V-3 50DF
Misc Info :
Comment :
Method : \\Etstarget\target\chem\dudejr.i\D020925A.b\D020925a.m
Meth Date : 09-Oct-2002 08:36 eich Quant Type: ESTD
Cal Date : 25-SEP-2002 13:54 Cal File: DUDE0025.D
Als bottle: 31
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/mL)	FINAL (ng/mL)
1 PFHS (299)	299	4.062	4.062	0.000	30746	931.455	932(M)
2 L16371 (500)	500	4.514	4.513	0.021	4077	1659.58	1660(M)
3 PFOS (499)	499	4.539	4.538	0.000	261522	44.2615	44.4
	499	4.411	4.195	0.216	6504	1699.12	1700

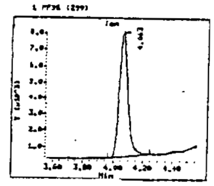
QC Flag Legend

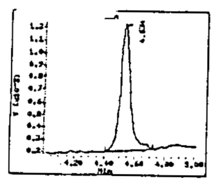
M - Compound response manually integrated.

Data File: \\Etstarget\target\chem\dudejr.i\D020925A.b\DUDE0029.D Page 2



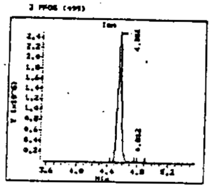
1 PFHS (299)





Data File: \\Etstarget\target\chem\dudejr.i\D020925A.b\DUDE0029.D Page 3

3 PFOS (499)



Data File: \\Etstarget\target\chem\dudejr.i\D020925A.b\DUDE0033.D Page 1
Report Date: 14-Oct-2002 10:27

3M Environmental Laboratory

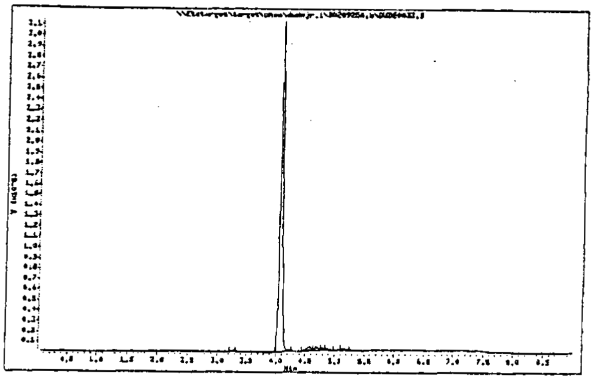
Data file : \\Etstarget\target\chem\dudejr.i\D020925A.b\DUDE0033.D
Lab Smp Id: E02-0970-43381
Inj Date : 25-SEP-2002 15:16
Operator : kje Inst ID: dudejr.i
Smp Info : TE3-EX-V-1 50DF
Misc Info :
Comment :
Method : \\Etstarget\target\chem\dudejr.i\D020925A.b\D020925a.m
Meth Date : 09-Oct-2002 08:36 eich Quant Type: ESTD
Cal Date : 25-SEP-2002 13:54 Cal File: DUDE0025.D
Als bottle: 35
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

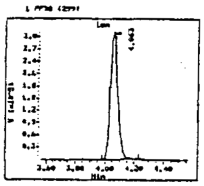
Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/mL)	FINAL (ng/mL)
1 PFHS (299)	299	4.062	4.062	0.000	1190651	76.4527	76.5
2 L16371 (500)	500	4.512	4.513	0.000	6559	1055.46	1060(M)
3 PFOS (499)	499	4.156	4.355	0.311	17619	1698.56	1700
	499	4.411	4.355	0.256	5144	1699.22	1700

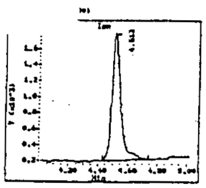
QC Flag Legend

M - Compound response manually integrated.

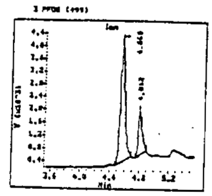
Page 2







Page 3



Data File: \\Etstarget\target\chem\dudejr.i\D020925A.b\DUDE0038.D Page 1
Report Date: 14-Oct-2002 10:27

3M Environmental Laboratory

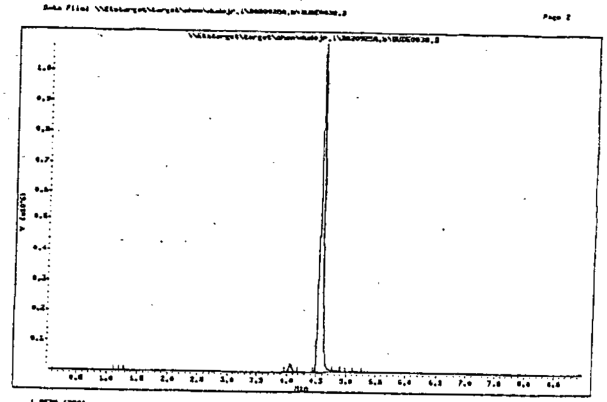
Data file : \\Etstarget\target\chem\dudejr.i\D020925A.b\DUDE0038.D
Lab Smp Id: E02-0968-43362
Inj Date : 25-SEP-2002 16:07
Operator : kje Inst ID: dudejr.i
Smp Info : TEJ-EX-PFOS-R-1 500F
Misc Info :
Comment :
Method : \\Etstarget\target\chem\dudejr.i\D020925A.b\D020925a.m
Meth Date : 09-Oct-2002 08:36 eich Quant Type: ESTD
Cal Date : 25-SEP-2002 13:54 Cal File: DUDE0025.D
Als bottle: 38
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

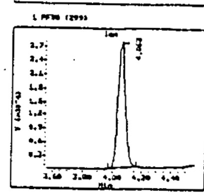
Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/mL)	FINAL (ng/mL)
1 PFHS (299)	299	4.362	4.462	0.000	57642	1.97671	2.56
2 L16371 (300)	500	4.520	4.511	0.007	1893	1065.73	1066(M)
3 PFOS (499)	499	4.535	4.556	0.000	1306547	276.604	171

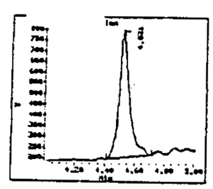
QC Flag Legend

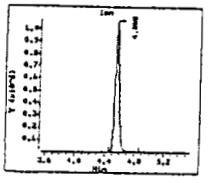
M - Compound response manually integrated.

Page 2









Data File: \\Etstarget\target\chem\itchy.i\I020926.b\ITCHY028.D Page 1
Report Date: 14-Oct-2002 09:39

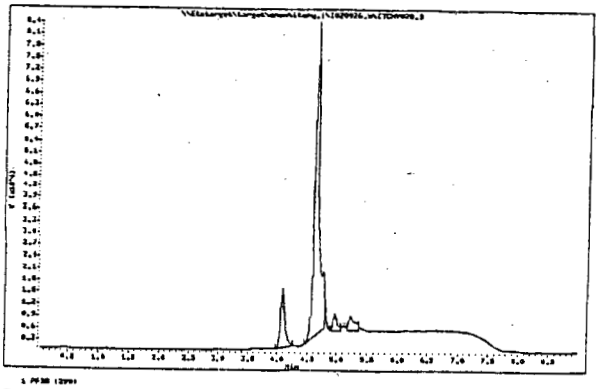
3M Environmental Laboratory

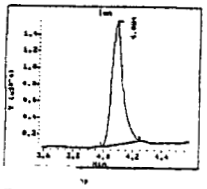
Data file : \\Etstarget\target\chem\itchy.i\I020926.b\ITCHY028.D
Lab Smp Id: E02-0895-42978
Inj Date : 26-SEP-2002 19:38
Operator : kje Inst ID: itchy.i
Smp Info : PFOS-2
Misc Info :
Comment :
Method : \\Etstarget\target\chem\itchy.i\I020926.b\I020926.m
Meth Date : 09-Oct-2002 09:21 eich Quant Type: ESTD
Cal Date : 26-SEP-2002 18:45 Cal File: ITCHY023.D
Ale bottle: 22
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: WL9559

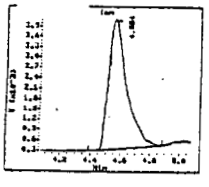
Compounds	Quant Ion Mass	RT	Exp RT	Dlt RT	Response	Concentrations On-Column (ng/mL)	Concentrations Final (ng/mL)
1 PFHS (Spk)	399	4.003	4.003	0.000	76213	1670.05	1670
2 L16271 (Spk)	369	4.383	4.373	-0.010	23117	6700.53	6700(M)
3 PFOS (Cal)	499	4.621	4.621	0.000	497197	5.60869	5.61

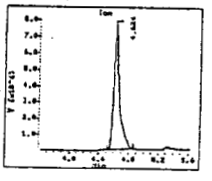
QC Flag Legend

M - Compound response manually integrated.









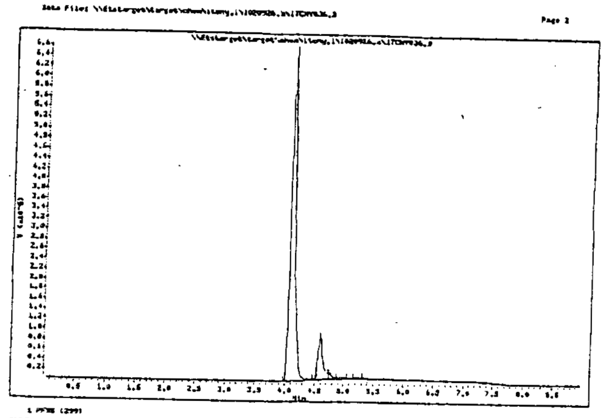
Data File: \\Etstarget\target\chem\itchy.i\I020926.b\ITCHY036.D Page 1
Report Date: 14-Oct-2002 09:59

3M Environmental Laboratory

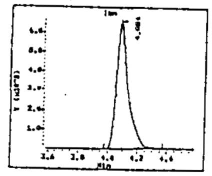
Data file : \\Etstarget\target\chem\itchy.i\I020926.b\ITCHY036.D
Lab Smp Id: E02-0896-42989
Inj Date : 26-SEP-2002 21:02
Operator : kje Inst ID: itchy.i
Smp Info : PFBS-1
Misc Info :
Comment :
Method : \\Etstarget\target\chem\itchy.i\I020926.b\I020926.m
Meth Date : 09-Oct-2002 09:22 eich Quant Type: ESTD
Cal Date : 26-SEP-2002 18:45 Cal File: ITCHY023.D
Als bottle: 29
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

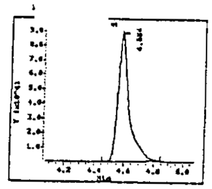
Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/mL)	FINAL (ng/mL)
1 PFHS (299)	299	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible] (500)	500	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
3 PFOS (499)	499	[illegible]	[illegible]	[illegible]	70345	[illegible]	[illegible]

Data File: \\Etstarget\target\chem\itchy.i\I020926.b\ITCHY036.D Page 2



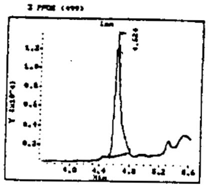
1 PFHS (299)





Data File: \\Etstarget\target\chem\itchy.i\I020926.b\ITCHY036.D Page 3

3 PFOS (499)



Data File: \\Etstarget\target\chem\itchy.i\I020926.b\ITCHY042.D Page 1
Report Date: 14-Oct-2002 10:00

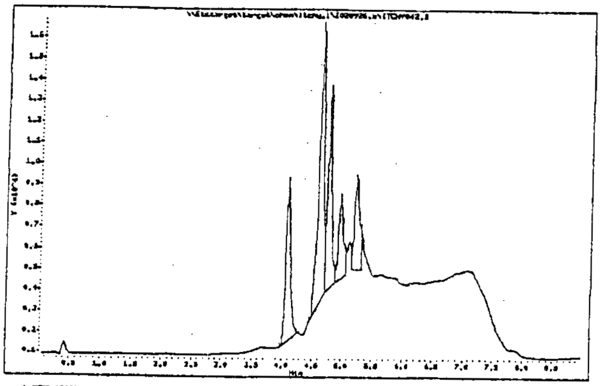
3M Environmental Laboratory

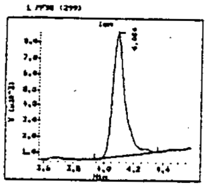
Data file : \\Etstarget\target\chem\itchy.i\I020926.b\ITCHY042.D
Lab Smp Id: E02-0839-42702
Inj Date : 26-SEP-2002 22:05
Operator : Inst ID: itchy.i
Smp Info :
Misc Info :
Comment :
Method : \\Etstarget\target\chem\itchy.i\I020926.b\I020926.m
Meth Date : 09-Oct-2002 09:22 eich Quant Type: ESTD
Cal Date : 26-SEP-2002 18:45 Cal File: ITCHY023.D
Als bottle: 33
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

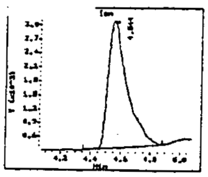
Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/mL)	FINAL (ng/mL)
1 PFHS (299)	299	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible](M)
2 [illegible] (500)	500	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible](M)
3 PFOS (499)	499	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible](M)

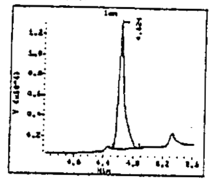
QC Flag Legend

M - Compound response manually integrated.









Data File: \\Etstarget\target\chem\itchy.i\I020926.b\ITCHY049.D Page 1
Report Date: 14-Oct-2002 10:00

3M Environmental Laboratory

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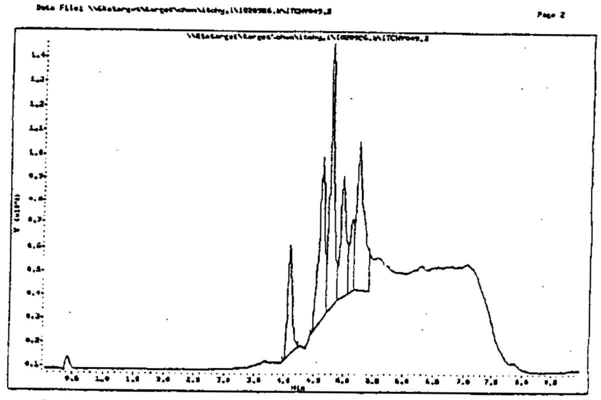
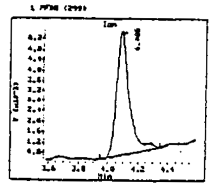
Inj Date : 26-SEP-2002 23:19
Operator : kje Inst ID: itchy.i
Smp Info : FC807-1
Misc Info :
Comment :
Method : \\Etstarget\target\chem\itchy.i\I020926.b\I020926.m
Meth Date : 09-Oct-2002 09:22 eicb Quant Type: ESTD
Cal Date : 26-SEP-2002 18:45 Cal File: ITCHY023.D
Als bottle: 39
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

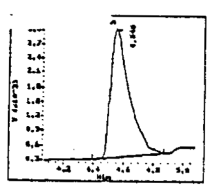
Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/ml)	FINAL (ng/ml)
1 PFHS (299)	299	4.404	4.401	0.003	34607	1672.18	1676(M)
2 L46371 (300)	300	4.144	4.173	-0.029	22401	8760.06	8700(M)
3 PFOS (499)	499	4.434	4.431	0.003	10492	2156.56	1166(M)

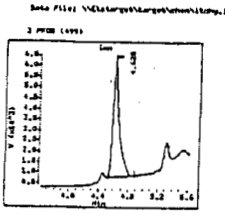
QC Flag Legend

M - Compound response manually integrated.









3M Environmental Laboratory

Data file : \\Et\target\target\chem\dudejr.i\D020924.b\DUDE0037.D
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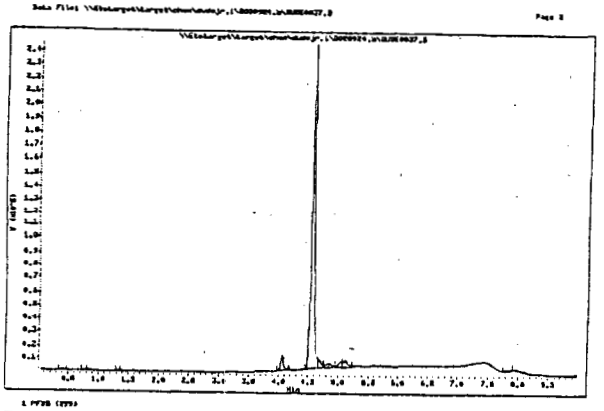
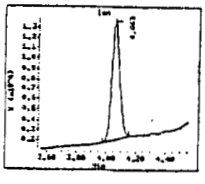
Operator : kje Inst ID: dudejr.i
Smp Info : TSI-EX-PFOS-R-1 50DF
Misc Info :
Comment :
Method : \\Et\target\target\chem\dudejr.i\D020924.b\D020924.m
Meth Date : 09-Oct-2002 08:07 eich Quant Type: ESTD
Cal Date : 24-SEP-2002 17:55 Cal File: DUDE0024.D
Als bottle: 26
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

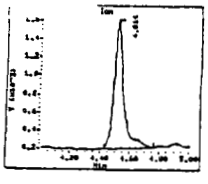
Compound	Quant Ion	RT	Exp RT	Dlt RT	Response	Conc (ng/mL)	Final (ng/mL)
1 PFOS (299)	299	4.662	4.656	0.006	43557	377.199	376
2 L14371 (500)	500	4.353	4.366	-0.007	5263	2420.61	2436(M)
3 PFOS (499)	499	4.565	4.565	0.007	752609	20.1197	19.2

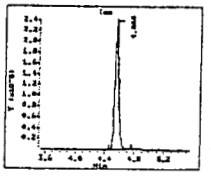
QC Flag Legend

M - Compound response manually integrated.









Data File: \\Etstarget\target\chem\dudejr.i\D020924.b\DUDE0038.D Page 1
Report Date: 14-Oct-2002 10:15

3M Environmental Laboratory

Data file : \\Etstarget\target\chem\dudejr.i\D020924.b\DUDE0038.D
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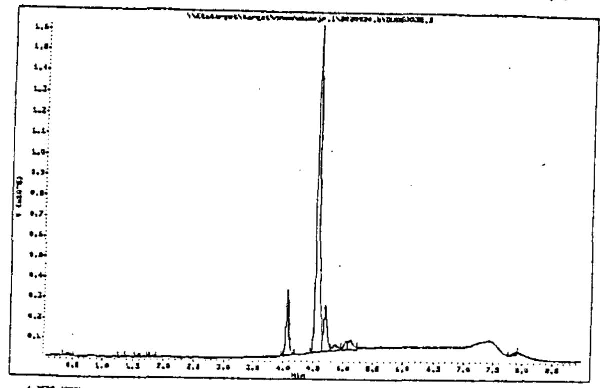
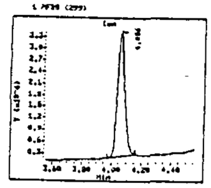
Inj Date : 24-SEP-2002 20:22
Operator : kje Inst ID: dudejr.i
Smp Info : TE-EX-PFOS-V-2
Misc Info :
Comment :
Method : \\Etstarget\target\chem\dudejr.i\D020924.b\D020924.m
Meth Date : 09-Oct-2002 08:07 eich Quant Type: ESTD
Cal Date : 24-SEP-2002 17:55 Cal File: DUDE0024.D
Als bottle: 27
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

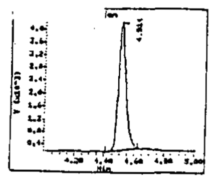
Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/mL)	FINAL (ng/mL)
1 PFHS (399)	399	4.054	4.554	0.500	113616	3.74396	3.74
2 L46371 (544)	544	4.313	4.306	0.007	14686	1437.71	1438
3 PFOS (499)	499	4.366	4.348	0.018	337690	13.7736	33.1

Data File: \\Etstarget\target\chem\dudejr.i\D020924.b\DUDE0038.D Page 2



1 PFHS (399)





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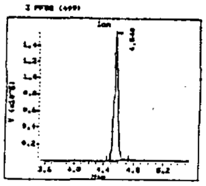
3 PFOS (499)



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Report Date: 14-Oct-2002 10:15

3M Environmental Laboratory

Data file : \\Etstarget\target\chem\dudejr.i\D020924.b\DUDE0041.D
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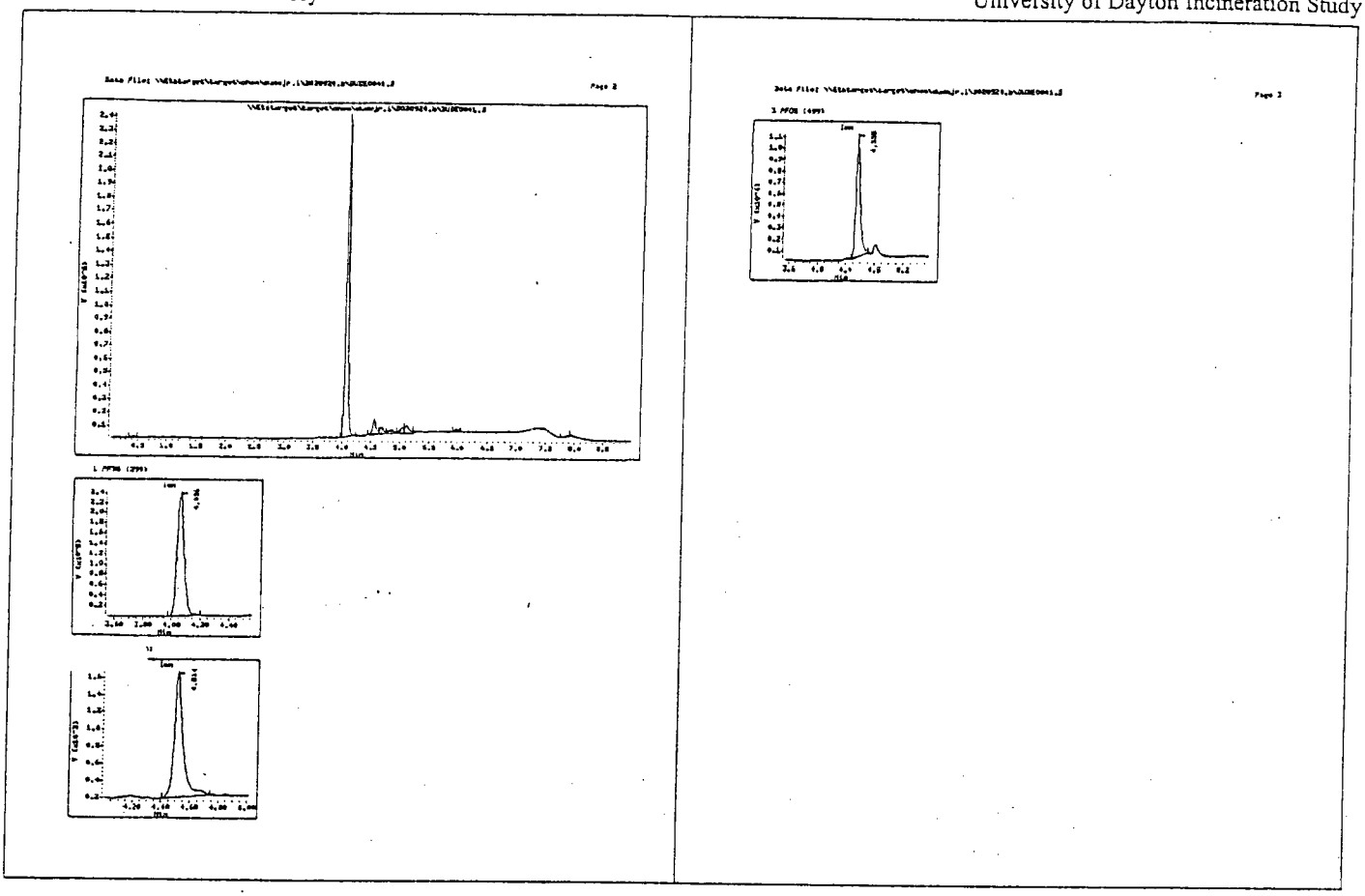
Inj Date : 24-SEP-2002 20:54
Operator : kje Inst ID: dudejr.i
Smp Info : TE3-EX-V-3 500F
Misc Info :
Comment :
Method : \\Etstarget\target\chem\dudejr.i\D020924.b\D020924.m
Meth Date : 09-Oct-2002 08:07 eich Quant Type: ESTD
Cal Date : 24-SEP-2002 17:55 Cal File: DUDE0024.D
Als bottle: 30
Dil Factor: 1.00000
Integrator: Falcon Compound Sublist: all.sub
Target Version: 4.10
Processing Host: W19559

Compounds	QUANT SIG MASS	RT	EXP RT	DLT RT	RESPONSE	CONCENTRATIONS ON-COLUMN (ng/mL)	FINAL (ng/mL)
1 PFHS (399)	399	4.456	4.456	0.000	419499	30.1990	30.2
2 L46371 (544)	544	4.313	4.306	0.007	4426	3420.40	3420(M)
3 PFOS (499)	499	4.355	4.348	0.007	16522	356.601	356

QC Flag Legend

M - Compound response manually integrated.



Appendix 5

Spreadsheet Linking the UDRI Combustion Tests with the 3M Analytical Results

Spreadsheet linking UDRI Thermal Testing and 3M Analytical Results

3M Sample Number	Date Sampled	UDRI Sample Description	Test*	Detailed Sample Description
E02-0821-42516	7/30/2002	WT-DT-1	5.2	Desktop wipe test before Test 2
E02-0821-42517	7/30/2002	WT-BT-1	5.2	Bench top wipe test before Test 2
E02-0821-42518	7/30/2002	WT-BLK-1	5.2	Wipe test blank for before Test 2
E02-0821-42519	7/30/2002	PFOS 1	5.2	1st extraction of PFOS spike
E02-0821-42520	7/30/2002	PFOS 2	5.2	2nd extraction of PFOS spike
E02-0821-42521	7/30/2002	PFBS 1	5.2	1st extraction of PFBS spike
E02-0821-42522	7/30/2002	PFBS 2	5.2	2nd extraction of PFBS spike
E02-0821-42523	7/30/2002	PFS - BLK	5.2	Solvent Blank for PFOS and PFBS extractions
E02-0821-42524	7/30/2002	WT-BT-2	5.2	Bench top wipe test after Test 2
E02-0821-42525	7/30/2002	WT-BLK-2	5.2	Wipe test blank for after Test 2
E02-0820-42500	8/2/2002	HB1-600-1	5.3	1st PUF for heated blank Combustion at 600°C
E02-0820-42501	8/2/2002	HB1-600-2	5.3	2nd PUF for heated blank Combustion at 600°C
E02-0820-42502	8/2/2002	HB1-900-1	5.3	1st PUF for heated blank Combustion at 900°C
E02-0820-42503	8/2/2002	HB1-900-2	5.3	2nd PUF for heated blank Combustion at 900°C
E02-0820-42504	8/2/2002	HB1-BLK-PUF	5.3	PUF blank for heated blank Combustion
E02-0820-42505	8/2/2002	HB1-1	5.3	1st extraction for heated blank Combustion
E02-0820-42506	8/2/2002	HB1-2	5.3	2nd extraction for heated blank Combustion
E02-0820-42507	8/2/2002	HB1-BLK	5.3	Extraction blank for heated blank Combustion
E02-0820-42508	8/2/2002	WT-BT-3	5.3	Wipe test for bench top after heated blank Combustion
E02-0820-42509	8/2/2002	WT-DT-3	5.3	Wipe test for desktop after heated blank Combustion
E02-0820-42510	8/2/2002	WT-BLK-3	5.3	Wipe test blank after heated blank Combustion
E02-0822-42526	8/5/2002	-600-1	5.4.1	1st PUF for Combustion at 600°C
E02-0822-42527	8/5/2002	-600-2	5.4.1	2nd PUF for Combustion at 600°C
E02-0822-42528	8/5/2002	-900-1	5.4.1	1st PUF for Combustion at 900°C
E02-0822-42529	8/5/2002	-900-2	5.4.1	2nd PUF for Combustion at 900°C
E02-0822-42530	8/5/2002	-BLK PUF	5.4.1	PUF blank for Combustion
E02-0822-42531	8/5/2002	-1	5.4.1	1st extraction for Combustion
E02-0822-42532	8/5/2002	-2	5.4.1	2nd extraction for Combustion
E02-0822-42533	8/5/2002	-BLK LIQ	5.4.1	Extraction blank for Combustion
E02-0822-42534	8/5/2002	WT-BT-4-1	5.4.1	Wipe test for bench top after Combustion
E02-0822-42535	8/5/2002	WT-DT-4-1	5.4.1	Wipe test for desktop after Combustion
E02-0822-42536	8/5/2002	WT-BLK-4-1	5.4.1	Wipe test blank after ombustion
E02-0839-42697	8/7/2002	-600-1	5.4.2	1st PUF for Combustion at 600°C
E02-0839-42698	8/7/2002	-600-2	5.4.2	2nd PUF for Combustion at 600°C
E02-0839-42699	8/7/2002	-900-1	5.4.2	1st PUF for Combustion at 900°C
E02-0839-42700	8/7/2002	-900-2	5.4.2	2nd PUF for Combustion at 900°C
E02-0839-42701	8/7/2002	-BLK-PUF	5.4.2	PUF blank for Combustion
E02-0839-42702	8/7/2002	-1	5.4.2	1st extraction for Combustion
E02-0839-42703	8/7/2002	-2	5.4.2	2nd extraction for Combustion

Spreadsheet linking UDRI Thermal Testing and 3M Analytical Results

E02-0839-42704	8/7/2002	-BLK	5.4.2	Extraction blank for Combustion
E02-0839-42705	8/7/2002	WT-BT-4-2	5.4.2	Wipe test for bench top after Combustion
E02-0839-42706	8/7/2002	WT-DT-4-2	5.4.2	Wipe test for desktop after Combustion
E02-0839-42707	8/7/2002	WT-BLK-4-2	5.4.2	Wipe test blank after Combustion
E02-0840-42708	8/9/2002	FC1395-600-1	5.4.3	1st PUF for FC-1395 Combustion at 600°C
E02-0840-42709	8/9/2002	FC1395-600-2	5.4.3	2nd PUF for FC-1395 Combustion at 600°C
E02-0840-42710	8/9/2002	FC1395-900-1	5.4.3	1st PUF for FC-1395 Combustion at 900°C
E02-0840-42711	8/9/2002	FC1395-900-2	5.4.3	2nd PUF for FC-1395 Combustion at 900°C
E02-0840-42712	8/9/2002	FC1395-BLK-PUF	5.4.3	PUF blank for FC-1395 Combustion
E02-0840-42714	8/9/2002	FC1395-1	5.4.3	1st extraction for FC-1395 Combustion
E02-0840-42715	8/9/2002	FC1395-2	5.4.3	2nd extraction for FC-1395 Combustion
E02-0840-42716	8/9/2002	FC1395-BLK	5.4.3	Extraction blank for FC-1395 Combustion
E02-0840-42717	8/9/2002	WT-BT-4-3	5.4.3	Wipe test for bench top after FC-1395 Combustion
E02-0840-42718	8/9/2002	WT-DT-4-3	5.4.3	Wipe test for desktop after FC-1395 Combustion
E02-0840-42719	8/9/2002	WT-BLK-4-3	5.4.3	Wipe test blank after FC-1395 Combustion
E02-0867-42903	8/20/2002	FC807-600-1	5.4.4	1st PUF for FC-807 Combustion at 600°C
E02-0867-42904	8/20/2002	FC807-600-2	5.4.4	2nd PUF for FC-807 Combustion at 600°C
E02-0867-42905	8/20/2002	FC807-69BLK	5.4.4	Blank Combustion between 600 and 900°C
E02-0867-42906	8/20/2002	FC807-900-1	5.4.4	1st PUF for FC-807 Combustion at 900°C
E02-0867-42907	8/20/2002	FC807-900-2	5.4.4	2nd PUF for FC-807 Combustion at 900°C
E02-0867-42908	8/20/2002	FC807-BLK-PUF	5.4.4	PUF blank for FC-807 Combustion
E02-0867-42909	8/20/2002	FC807-0	5.4.4	Valve and Extended Tubing Extraction after 600°C FC-807 Combustion
E02-0867-42910	8/20/2002	FC807-1	5.4.4	1st extraction for FC-807 Combustion
E02-0867-42911	8/20/2002	FC807-2	5.4.4	2nd extraction for FC-807 Combustion
E02-0867-42912	8/20/2002	FC807-BLK	5.4.4	Extraction blank for FC-807 Combustion
E02-0867-42913	8/20/2002	WT-BT-4-4	5.4.4	Wipe test for bench top after FC-807 Combustion
E02-0867-42914	8/20/2002	WT-DT-4-4	5.4.4	Wipe test for desktop after FC-807 Combustion
E02-0867-42915	8/20/2002	WT-BLK-4-4	5.4.4	Wipe test blank after FC-807 Combustion
E02-0898-42995	8/21/2002	-600-1	5.4.5	1st PUF for Combustion at 600°C
E02-0898-42996	8/21/2002	-600-2	5.4.5	2nd PUF for Combustion at 600°C
E02-0898-42997	8/21/2002	-69BLK	5.4.5	Blank Combustion between 600 and 900°C
E02-0898-42998	8/21/2002	-900-1	5.4.5	1st PUF for Combustion at 900°C
E02-0898-42999	8/21/2002	-900-2	5.4.5	2nd PUF for Combustion at 900°C
E02-0898-43000	8/21/2002	-BLK-PUF	5.4.5	PUF blank for In Combustion
E02-0898-43001	8/21/2002	-1	5.4.5	1st extraction for Combustion
E02-0898-43002	8/21/2002	-2	5.4.5	2nd extraction for Combustion
E02-0898-43003	8/21/2002	-BLK	5.4.5	Extraction blank for Combustion
E02-0898-43004	8/21/2002	WT-BT-4-5	5.4.5	Wipe test for bench top after Combustion
E02-0898-43005	8/21/2002	WT-DT-4-5	5.4.5	Wipe test for desktop after Combustion
E02-0898-43006	8/21/2002	WT-BLK-4-5	5.4.5	Wipe test blank after Combustion
E02-0896-42983	8/22/2002	PFBS-600-1	5.4.6	1st PUF for PFBS Combustion at 600°C
E02-0896-42984	8/22/2002	PFBS-600-2	5.4.6	2nd PUF for PFBS Combustion at 600°C

Spreadsheet linking UDRI Thermal Testing and 3M Analytical Results

E02-0896-42985	8/22/2002	PFBS-69BLK	5.4.6	Blank Combustion between 600 and 900°C
E02-0896-42986	8/22/2002	PFBS-900-1	5.4.6	1st PUF for PFBS Combustion at 900°C
E02-0896-42987	8/22/2002	PFBS-900-2	5.4.6	2nd PUF for PFBS Combustion at 900°C
E02-0896-42988	8/22/2002	PFBS-BLK-PUF	5.4.6	PUF blank for PFBS Combustion
E02-0896-42989	8/22/2002	PFBS-1	5.4.6	1st extraction for PFBS Combustion
E02-0896-42990	8/22/2002	PFBS-2	5.4.6	2nd extraction for PFBS Combustion
E02-0896-42991	8/22/2002	PFBS-BLK	5.4.6	Extraction blank for PFBS Combustion
E02-0896-42992	8/22/2002	WT-BT-4-6	5.4.6	Wipe test for bench top after PFBS Combustion
E02-0896-42993	8/22/2002	WT-DT-4-6	5.4.6	Wipe test for desktop after PFBS Combustion
E02-0896-42994	8/22/2002	WT-BLK-4-6	5.4.6	Wipe test blank after PFBS Combustion
E02-0895-42970	8/26/2002	PFOS-600-1	5.4.7	1st PUF for PFOS Combustion at 600°C
E02-0895-42971	8/26/2002	PFOS-600-2	5.4.7	2nd PUF for PFOS Combustion at 600°C
E02-0895-42972	8/26/2002	PFOS-69BLK	5.4.7	Blank Combustion between 600 and 900°C
E02-0895-42973	8/26/2002	PFOS-900-1	5.4.7	1st PUF for PFOS Combustion at 900°C
E02-0895-42974	8/26/2002	PFOS-900-2	5.4.7	2nd PUF for PFOS Combustion at 900°C
E02-0895-42975	8/26/2002	PFOS-BLK-PUF	5.4.7	PUF blank for PFOS Combustion
E02-0895-42976	8/26/2002	PFOS-0	5.4.7	Valve and Extended Tubing Extraction after 600°C PFOS Combustion
E02-0895-42977	8/26/2002	PFOS-1	5.4.7	1st extraction for PFOS Combustion
E02-0895-42978	8/26/2002	PFOS-2	5.4.7	2nd extraction for PFOS Combustion
E02-0895-42979	8/26/2002	PFOS-BLK	5.4.7	Extraction blank for PFOS Combustion
E02-0895-42980	8/26/2002	WT-BT-4-7	5.4.7	Wipe test for bench top after PFOS Combustion
E02-0895-42981	8/26/2002	WT-DT-4-7	5.4.7	Wipe test for desktop after PFOS Combustion
E02-0895-42982	8/26/2002	WT-BLK-4-7	5.4.7	Wipe test blank after PFOS Combustion
E02-0899-43007	8/27/2002	HB2-600-1	5.6	1st PUF for 2nd heated blank Combustion at 600°C
E02-0899-43008	8/27/2002	HB2-600-2	5.6	2nd PUF for 2nd heated blank Combustion at 600°C
E02-0899-43009	8/27/2002	HB2-900-1	5.6	1st PUF for 2nd heated blank Combustion at 900°C
E02-0899-43010	8/27/2002	HB2-900-2	5.6	2nd PUF for 2nd heated blank Combustion at 900°C
E02-0899-43011	8/27/2002	HB2-BLK-PUF	5.6	PUF blank for 2nd heated blank Combustion
E02-0899-43012	8/27/2002	HB2-1	5.6	1st extraction for 2nd heated blank Combustion
E02-0899-43013	8/27/2002	HB2-2	5.6	2nd extraction for 2nd heated blank Combustion
E02-0899-43014	8/27/2002	HB2-BLK	5.6	Extraction blank for 2nd heated blank Combustion
E02-0899-43015	8/27/2002	WT-BT-HB2	5.6	Wipe test for bench top after 2nd heated blank Combustion
E02-0899-43016	8/27/2002	WT-DT-HB2	5.6	Wipe test for desktop after 2nd heated blank Combustion
E02-0899-43017	8/27/2002	WT-BLK-HB2	5.6	Wipe test blank after 2nd heated blank Combustion
E02-0916-43081	8/28/2002	TE-1	5.7.1	1st PUF 1st Transfer Efficiency
E02-0916-43082	8/28/2002	TE-2	5.7.1	2nd PUF : 1st Transfer Efficiency
E02-0916-43083	8/28/2002	PFBS-TE-1	5.7.1	1st PUF PFBS 1st Transfer Efficiency
E02-0916-43084	8/28/2002	PFBS-TE-2	5.7.1	2nd PUF PFBS 1st Transfer Efficiency
E02-0916-43085	8/28/2002	PFOS-TE-1	5.7.1	1st PUF PFOS 1st Transfer Efficiency
E02-0916-43086	8/28/2002	PFOS-TE-2	5.7.1	2nd PUF PFOS 1st Transfer Efficiency
E02-0916-43087	8/28/2002	TE-BLK	5.7.1	PUF Blank for 1st Transfer Efficiency
E02-0916-43088	8/28/2002	WT-DT-6	5.7.1	Wipe Test Desktop 1st Transfer Efficiency

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E02-0916-43089	8/28/2002	WT-BLK-6	5.7.1	Wipe Test Blank 1st Transfer Efficiency
E02-0917-43090	8/30/2002	TE2-1	5.7.2	1st PUF 2nd Transfer Efficiency
E02-0917-43091	8/30/2002	TE2-2	5.7.2	2nd PUF 2nd Transfer Efficiency
E02-0917-43092	8/30/2002	PFBS-TE2-1	5.7.2	1st PUF PFBS 2nd Transfer Efficiency
E02-0917-43093	8/30/2002	PFBS-TE2-2	5.7.2	2nd PUF PFBS 2nd Transfer Efficiency
E02-0917-43094	8/30/2002	PFOS-TE2-1	5.7.2	1st PUF PFOS 2nd Transfer Efficiency
E02-0917-43095	8/30/2002	PFOS-TE2-2	5.7.2	2nd PUF PFOS 2nd Transfer Efficiency
E02-0917-43096	8/30/2002	TE2-BLK	5.7.2	PUF Blank for 2nd Transfer Efficiency
E02-0917-43097	8/30/2002	WT-BT-TE2	5.7.2	Wipe Test Bench top 2nd Transfer Efficiency
E02-0917-43098	8/30/2002	WT-DT-TE2	5.7.2	Wipe Test Desktop 2nd Transfer Efficiency
E02-0917-43099	8/30/2002	WT-BLK-TE2	5.7.2	Wipe Test Blank 2nd Transfer Efficiency
E02-0917-43100	8/30/2002	-TE2X-1	5.7.2	1st extraction 2nd Transfer Efficiency
E02-0917-43101	8/30/2002	-TE2X-2	5.7.2	2nd extraction 2nd Transfer Efficiency
E02-0917-43102	8/30/2002	-TE2X-BLK	5.7.2	Blank extraction 2nd Transfer Efficiency
E02-0917-43103	8/30/2002	PFBS-TE2X-1	5.7.2	1st extraction PFBS 2nd Transfer Efficiency
E02-0917-43104	8/30/2002	PFBS-TE2X-2	5.7.2	2nd extraction PFBS 2nd Transfer Efficiency
E02-0917-43105	8/30/2002	PFBS-TE2X-BLK	5.7.2	Blank extraction PFBS 2nd Transfer Efficiency
E02-0917-43106	8/30/2002	PFOS-TE2X-1	5.7.2	1st extraction PFOS 2nd Transfer Efficiency
E02-0917-43107	8/30/2002	PFOS-TE2X-2	5.7.2	2nd extraction PFOS 2nd Transfer Efficiency
E02-0917-43108	8/30/2002	PFOS-TE2X-BLK	5.7.2	Blank extraction PFOS 2nd Transfer Efficiency
E02-0926-43141	9/6/2002	NHB-1		1st extraction for non-heated blank
E02-0926-43142	9/6/2002	NHB-2		2nd extraction for non-heated blank
E02-0926-43143	9/6/2002	NHB-BLK		Extraction blank for non-heated blank
E02-0926-43144	9/6/2002	WT-BT-NHB		Wipe test on bench top after non-heated blank
E02-0926-43145	9/6/2002	WT-BLK-NHB		Wipe test blank after non-heated blank
E02-0970-43377	9/20/2002	PFBS-AIR-TE3-1	5.7.3	1st PUF for PFBS in air 3rd Transfer Efficiency
E02-0970-43378	9/20/2002	PFBS-AIR-TE3-2	5.7.3	2nd PUF for PFBS in air 3rd Transfer Efficiency
E02-0970-43379	9/20/2002	TE3-EX-R-1	5.7.3	1st Extraction of Reactor and Transfer line for 3rd Transfer Efficiency of PFBS in air
E02-0970-43380	9/20/2002	TE3-EX-R-2	5.7.3	2nd Extraction of Reactor and Transfer line for 3rd Transfer Efficiency of PFBS in air
E02-0970-43381	9/20/2002	TE3-EX-V-1	5.7.3	1st Extraction of Valve & Short Transfer line for 3rd Transfer Efficiency of PFBS in air
E02-0970-43382	9/20/2002	TE3-EX-V-2	5.7.3	2nd Extraction of Valve & Short Transfer line for 3rd Transfer Efficiency of PFBS in air
E02-0970-43383	9/20/2002	PFBS-HE-TE3-1	5.7.3	1st PUF for PFBS in He 3rd Transfer Efficiency
E02-0970-43384	9/20/2002	PFBS-HE-TE3-2	5.7.3	2nd PUF for PFBS in He 3rd Transfer Efficiency
E02-0970-43385	9/20/2002	TE3-EX-R-3	5.7.3	1st Extraction of Reactor and Transfer line for 3rd Transfer Efficiency of PFBS in He
E02-0970-43386	9/20/2002	TE3-EX-R-4	5.7.3	2nd Extraction of Reactor and Transfer line for 3rd Transfer Efficiency of PFBS in He
E02-0971-43387	9/20/2002	TE3-EX-V-3	5.7.3	1st Extraction of Valve & Short Transfer line for 3rd Transfer Efficiency of PFBS in He
E02-0971-43388	9/20/2002	TE3-EX-V-4	5.7.3	2nd Extraction of Valve & Short Transfer line for 3rd Transfer Efficiency of PFBS in He
E02-0971-43389	9/20/2002	WT-BT-TE3-PFBS	5.7.3	Wipe Test Bench top PFBS 3rd Transfer Efficiency
E02-0971-43390	9/20/2002	WT-DT-TE3-PFBS	5.7.3	Wipe Test Desktop PFBS 3rd Transfer Efficiency
E02-0971-43391	9/20/2002	WT-BLK-TE3-PFBS	5.7.3	Wipe Test Blank PFBS 3rd Transfer Efficiency
E02-0971-43392	9/20/2002	PFBS-BLK-TE3	5.7.3	PUF Blank for PFBS in air 3rd Transfer Efficiency
E02-0971-43393	9/20/2002	TE3-EX-BLK-1	5.7.3	1st Blank extraction for 3rd Transfer Efficiency

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E02-0969-43371	9/20/2002	PFOS-AIR-TE3-1	5.7.3	1st PUF for PFOS in air 3rd Transfer Efficiency
E02-0969-43372	9/20/2002	PFOS-AIR-TE3-2	5.7.3	2nd PUF for PFOS in air 3rd Transfer Efficiency
E02-0969-43373	9/20/2002	TE3-EX-PFOS-R-1	5.7.3	1st Extraction of Reactor and Transfer line for 3rd Transfer Efficiency of PFOS in air
EQ2-0969-43374	9/20/2002	TE3-EX-PFOS-R-2	5.7.3	2nd Extraction of Reactor and Transfer line for 3rd Transfer Efficiency of PFOS in air
E02-0969-43375	9/20/2002	TE3-EX-PFOS-V-1	5.7.3	1st Extraction of Valve & Short Transfer line for 3rd Transfer Efficiency of PFOS in air
E02-0969-43376	9/20/2002	TE3-EX-PFOS-V-2	5.7.3	2nd Extraction of Valve & Short Transfer line for 3rd Transfer Efficiency of PFBS in air
E02-0968-43360	9/20/2002	PFOS-HE-TE3-1	5.7.3	1st PUF for PFOS in He 3rd Transfer Efficiency
E02-0968-43361	9/20/2002	PFOS-HE-TE3-2	5.7.3	2nd PUF for PFOS in He 3rd Transfer Efficiency
E02-0968-43362	9/20/2002	TE3-EX-PFOS-R-3	5.7.3	1st Extraction of Reactor and Transfer line for 3rd Transfer Efficiency of PFOS in He
E02-0968-43363	9/20/2002	TE3-EX-PFOS-R-4	5.7.3	2nd Extraction of Reactor and Transfer line for 3rd Transfer Efficiency of PFOS in He
E02-0968-43364	9/20/2002	TE3-EX-PFOS-V-3	5.7.3	1st Extraction of Valve & Short Transfer line for 3rd Transfer Efficiency of PFOS in He
E02-0968-43365	9/20/2002	TE3-EX-PFOS-V-4	5.7.3	2nd Extraction of Valve & Short Transfer line for 3rd Transfer Efficiency of PFOS in He
E02-0968-43366	9/20/2002	TE3-EX-BLK-2	5.7.3	2nd Blank extraction for 3rd Transfer Efficiency
E02-0968-43367	9/20/2002	WT-BT-TE3-PFOS	5.7.3	Wipe Test Bench top PFOS 3rd Transfer Efficiency
E02-0968-43368	9/20/2002	WT-DT-TE3-PFOS	5.7.3	Wipe Test Desktop PFOS 3rd Transfer Efficiency
E02-0968-43369	9/20/2002	WT-BLK-TE3-PFOS	5.7.3	Wipe Test Blank PFOS 3rd Transfer Efficiency
E02-0968-43370	9/20/2002	PFOS-BLK-TE3	5.7.3	PUF Blank for PFOS in air 3rd Transfer Efficiency

* corresponds to section number in final report.