1 **APPENDIX B.1**
2 **GUIDELINE FOR THERMOGRAVIMETRIC ANALYSIS**
3
4 As described in Appendix C.2.3, thermogravimetric analysis will
5 be conducted as part of this testing program. An available
6 standard method (ASTM E 1868-02) has been adapted for conducting
7 this thermogravimetric analysis to determine the temperature
8 range required for gasification. Therefore, ASTM E 1868-02
9 "Standard Test Method for Loss-On-Drying by Thermogravimetry"
10 will be used as the guideline for conducting the analysis
11 described in Appendix C.2.3 with the following modifications for
12 this testing program:
13

Section	Modification
2.1	• Standard practices at the University of Dayton Research Institute (UDRI) may be used as references throughout the standard in place of the ASTM standards noted in this section as they are not needed for this testing program.
4.1	• The loss-on-drying value specified in the second through fifth sentences of this section will not be recorded as this value is not needed for this testing program.
7.1.3	• The programming rate of the furnace will be set at 10 to 25°C/min, rather than 5°C/min. Pursuant to section 11.6, the temperature program rate will be documented in the report. • The isothermal temperature within the range of 25 to 1000°C will be maintained ±3°C, rather than ±2°C.
7.1.4	• The specimen atmosphere control system will be capable of supplying dry air in addition to "inert dry gas (usually purified grade nitrogen)".
7.1.7	• The temperature program rate will be set at 10 to 25°C/min, rather than 5°C/min. Pursuant to section 11.6, the temperature program rate will be documented in the report. • The temperature program rate will be controlled to within the range of ±3°C/min, rather than ±0.1°C/min. • Within the range of 25 to 1000°C, the isothermal temperature will be maintained within ±3°C, rather than ±2°C.
11.4	• The mass of the test specimen noted in the first sentence of this section will be 0.005 to 5 mg, rather than 10±1 mg (i.e., 9 to 11 mg).

11.6	• The test specimen heating rate will be set at 10 to 25°C/min, rather than 5°C/min noted in the first sentence of this section. Pursuant to section 11.6, the temperature program rate will be documented in the report.
11.9	• Termination criteria will follow Test Method A as outlined in section 11.10.1.
11.10.1	• The "fixed period of test time" mentioned in this section will be set at 5 min.
11.10.1.1	• Loss-on-drying values will not be recorded.
12.1	• The loss-on-drying value will not be calculated.
13.1.1	• The "identification and description of the material being tested" will be consistent with the information known to the analyst.
13.1.5	• The loss-on-drying value will not be included in the report.
14.2	• This section is not applicable because the Test Method A termination criteria will be used.

14
15
16 **Reference**
17 ASTM E 1868-02 "Standard Test Method for Loss-On-Drying by
18 Thermogravimetry", ASTM International. For referenced ASTM
19 standards, visit the ASTM website, www.astm.org, or contact ASTM
20 Customer Service at service@astm.org. For Annual Book of ASTM
21 Standards volume information, refer to the standard's Document
22 Summary page on the ASTM website.

1 **APENDIX C.1**
2 **PFOA TRANSPORT TESTING**
3
4 C.1.1 Significance
5
6 Testing will be performed to verify that potential PFOA
7 emissions from the combustion testing described in Appendix
8 C.2 can be quantitatively transported from the high
9 temperature reactor into the exhaust gas sampling apparatus
10 (aqueous solution bubblers).
11
12 Acceptable PFOA transport will be demonstrated if the
13 transport efficiency (as computed in one or more of the
14 formulas below) is greater than or equal to 70%.
15
16 C.1.2 Experimental Plan
17
18 C.1.2.1 Base Plan
19
20 Transport of PFOA across the laboratory-scale thermal
21 reactor system described in Appendix C.2.4 and into the
22 exhaust gas bubblers described in Appendix D.1 will be
23 quantitatively determined as an indication of transport
24 from the high temperature reactor into the bubblers.
25
26 A PFOA standard of known purity greater than or equal to
27 97% will be gasified at 150 to 300 °C (based on
28 thermogravimetric analysis of PFOA) with transfer line and
29 reactor temperatures 0 to 150 °C higher than the
30 gasification temperature. With the exception of
31 temperature as noted above, the target operating conditions
32 for the high temperature reactor of the thermal reactor
33 system will be consistent with the conditions presented in
34 Table C.2-1 in Appendix C.2.4.
35
36 Three replicate transport efficiency test runs will be
37 conducted. A minimum of one blank run will be conducted
38 prior to each transport efficiency test run.
39
40 The sample size of the PFOA standard to be gasified will be
41 less than 5 mg. The reactor exhaust gas will be collected
42 into bubbler aqueous solution as described in Appendix D.1
43 (including an HPLC water rinse of the flexible tubing [used
44 to connect the thermal reactor system and the bubbler
45 assembly] into the aqueous solution composite), which will
46 be analyzed for PFOA as described in Appendix D.2. In
47 order to provide a second way of demonstrating quantitative

1　transport, this aqueous solution composite will also be
2　analyzed for total fluorine as described in Appendix D.3.
3　(Testing for total fluorine is included due to possibility
4　of thermal degradation of PFOA under transport test
5　conditions.) Therefore, for this transport testing the
6　amount of PFOA fed to the thermal reactor system will be
7　sufficiently high to assure that the total fluorine input
8　to the thermal reactor system will be greater than 140% of
9　the mass corresponding to the limit of quantitation (LOQ)
10　for total fluorine in the aqueous solution composite. (The
11　LOQ for total fluorine in aqueous solution is much higher
12　than the LOQ for PFOA in aqueous solution.)
13
14　The amount of PFOA and total fluorine in the thermal
15　reactor system exhaust gas will be determined via analysis
16　of the aqueous solution composite as noted above.
17
18　The amount of PFOA fed to the thermal reactor system will
19　be known based on measurement prior to gasification and
20　will be verified by weighing the pyroprobe insert cartridge
21　before and after each test run. The amount of fluorine
22　input to the system will be calculated from the amount of
23　PFOA fed, the known purity of the PFOA, and the known
24　fluorine fraction of the PFOA standard.
25
26　PFOA transport efficiency (TE) as a percentage will be
27　computed as follows:
28
29　% PFOA TE = mass of PFOA in aqueous solution composite * 100　　(1)
30　　　　　　　　　mass of PFOA fed to thermal reactor system
31
32　Total fluorine (TF) transport efficiency as a percentage
33　will be computed as follows:
34
35　% Total F TE = mass of total F in aqueous solution composite * 100　(2)
36　　　　　　　　　　mass of total F fed to thermal reactor system
37
38　C.1.2.2 Contingent Testing
39
40　If the transport efficiencies for both PFOA (equation 1)
41　and total fluorine (equation 2) are less than 70%, then
42　additional work will be performed. This additional work
43　will be performed in a step-wise fashion to determine if
44　consideration of one or more of the following procedural
45　revisions enables achievement of 70% transport efficiency
46　as follows:
47

Step 1. The flexible tubing between the thermal reactor system and the bubbler assembly from the experiment described in Section C.1.2.1 would be quantitatively rinsed with methanol. This methanol rinsate would be analyzed for PFOA (as described in Appendix D.2) and/or for total fluorine (as described in Appendix D.3). Revised transport efficiency (TE) as a percentage for PFOA (equation 3) and/or total fluorine (equation 4) would be computed by including the mass of analyte in the methanol rinse in the numerator as follows:

$$\% \text{ PFOA TE} = \frac{\text{mass}_{PFOA} \text{ out}}{\text{mass}_{PFOA} \text{ in}} * 100 \qquad (3)$$

where mass_{PFOA} out = mass of PFOA in bubbler aqueous solution composite + mass of PFOA in methanol rinse

and mass_{PFOA} in = mass of PFOA fed to thermal reactor system

$$\% \text{ Total F TE} = \frac{\text{mass}_{total\ F} \text{ out}}{\text{mass}_{total\ F} \text{ in}} * 100 \qquad (4)$$

where $\text{mass}_{total\ F}$ out = mass of total F in bubbler aqueous solution composite + mass of total F in methanol rinse

and $\text{mass}_{total\ F}$ in = calculated mass of total F in PFOA fed to thermal reactor system

Step 2 (if necessary) The experiment described in Section C.1.2.1 would be repeated with reagent(s) (e.g. NaOH) added to the bubbler aqueous solution to determine if reagent addition enhances analyte absorption, thereby improving transport efficiency. Transport efficiency would be calculated using equation (1) and/or (2) above. The impact of reagent addition on LOQ for PFOA analysis described in Appendix D.2 would be determined.

1   C.1.3 Reporting of Results
2
3   Following completion of PFOA transport testing as described
4   in this appendix and prior to beginning incineration
5   testing described in Appendix C.2, a letter report will be
6   submitted to EPA with the transport efficiency result(s)
7   and indication of what contingent testing, if any, was
8   performed.
9
10 If Appendix C.2 incineration testing is performed, the
11 detailed results of Appendix C.1 transport testing will be
12 included in the test report for Appendix C.2 incineration
13 testing described in Appendix C.2.5. If Appendix C.2
14 incineration testing is not performed, the detailed results
15 of Appendix C.1 transport testing will be provided in a
16 test report for Appendix C.1 transport testing.

1   **APPENDIX C.2**
2   **INCINERATION TESTING**
3
4   **C.2.1 ELEMENTAL ANALYSIS**
5
6   C.2.1.1 Introduction
7
8   Elemental analysis as described in Section C.2.1 will be
9   performed for each test substance composite to aid in
10 preparation for combustion testing described in Section
11 C.2.4.
12
13 As Kissa (1998) points out, technique strongly affects
14 analytical results for fluorinated organic compounds such
15 as fluorinated surfactants and fluorinated polymers due to
16 the carbon-fluorine bond:
17
18   Fluorine in organic compounds is usually
19   determined by converting organic fluorine to an
20   inorganic fluoride. Various combustion methods
21   are routinely used for this purpose. However,
22   the carbon-fluorine bond is exceptionally strong,
23   and extremely vigorous conditions are needed for
24   a quantitative mineralization. Conventional
25   combustion conditions used for the determination
26   of carbon and hydrogen in nonfluorinated organic
27   compounds are not adequate for a quantitative
28   analysis of fluorinated surfactants.
29
30 Therefore, total fluorine analysis will be performed using
31 "extremely vigorous conditions" as described in Section
32 C.2.1.2, and the commercially available conventional
33 technique used for empirical determination of carbon and
34 hydrogen content (described in Section C.2.1.3) will
35 provide estimated values.
36
37 C.2.1.2 Total Fluorine
38
39 Each test substance composite will be characterized via
40 analysis of total fluorine content.
41
42 Based on manufacturing process knowledge, the levels of
43 total fluorine in the components of test substance
44 composites are orders of magnitude higher than the
45 potential trace level of inorganic fluoride in these
46 materials. Therefore, for this test program, the total
47 organic fluorine value for each test substance composite

1 will be considered to be the same as the total fluorine
2 value.
3
4 Total fluorine content will be measured via the Wickbold
5 Torch method; see Appendix D.3.
6
7 C.2.1.3 Carbon and Hydrogen
8
9 In order to provide information for stoichiometric
10 calculations in Section C.2.2, the carbon and hydrogen
11 content of each test substance composite is needed. Based
12 on manufacturing process knowledge of the polymers in this
13 program, levels of sulfur, and nitrogen are expected to be
14 less than 0.1% and to thereby have negligible effect on
15 stoichiometric calculations.
16
17 C.2.1.3.1 Theoretical Determination
18
19 Where the elemental composition of a test substance
20 composite is known from the identity of the components in a
21 given composite, the carbon and hydrogen content of the
22 test substance composite can be calculated.
23
24 For example, where each of the components of a test
25 substance composite are polytetrafluoroethylene (PTFE), the
26 carbon and hydrogen can be determined knowing the molecular
27 formula for PTFE is $(C_2F_4)_n$ as follows:
28

	number	atomic weight	weight %
carbon (C)	2	12	24
hydrogen (H)	0	1	0
fluorine (F)	4	19	76
total			100

29
30 C.2.1.3.2 Empirical Determination
31
32 Where compositional information on carbon and hydrogen
33 content is not known from the identity of the components in
34 a given composite, each such test substance composite will
35 be analyzed for carbon and hydrogen.
36
37 As noted in Section C.2.1.1, empirical determination of
38 carbon in test substance composites via commercially
39 available conventional techniques is expected to
40 underestimate the carbon content of the test substance
41 composites due to the strength of the carbon-fluorine bond.
42 Similarly, empirical determination of hydrogen in test

1 substance composites via commercially available
2 conventional techniques is expected to overestimate the
3 hydrogen content of the test substance composites.
4
5 The carbon content of the test substance composite can be
6 measured by determining the carbon dioxide (CO_2) generated
7 by the oxidation of the sample. This oxidation may be
8 accomplished by high temperature combustion, catalytic
9 combustion, or wet chemical oxidation. The CO_2 is measured
10 directly by an infrared detector or a thermal conductivity
11 detector, via absorption into a suitable solution (e.g.,
12 potassium hydroxide) and gravimetric determination, or by
13 conversion to methane for measurement via a flame
14 ionization detector.
15
16 The hydrogen content of the sample can be determined by
17 difference with knowledge of the fluorine content and
18 carbon content of the sample where the moisture content and
19 chlorine content of the sample are negligible or known.
20 Alternatively, the hydrogen content of the sample is
21 measured by determining the water generated by high
22 temperature combustion of the sample. Measurement of water
23 in the combustion gas for this analysis may be accomplished
24 by techniques such as use of an infrared detector or
25 absorption on a dessicant with gravimetric determination.
26 With empirical hydrogen determination, it is important to
27 correct for the water in the combustion gas attributable to
28 the moisture content in the sample to obtain the hydrogen
29 content of the sample; see Section C.2.1.4.
30
31 Manufacturing process knowledge of the polymers will be
32 used to review the elemental analysis results and to form
33 the basis for interpreting non-detects. For example, if
34 the hydrogen analytical result for a perfluorinated polymer
35 is less than a quantitation limit of 0.1%, then the
36 analytical result will be replaced with 0.
37
38 C.2.1.4 Moisture
39
40 Where preparation (as described in Appendix A.4) for a
41 given test substance composite has involved dewatering, the
42 moisture (or solids) content of each such test substance
43 composite will be determined in order to provide a dry
44 basis for calculations as needed.
45
46 Moisture is determined by measuring the loss of weight of
47 the sample when heated under controlled conditions. A

1 representative sample is weighed and placed in a crucible
2 (or dish) and evaporated to dryness in an air or nitrogen
3 atmosphere at a defined temperature setpoint (e.g., 103 $^\circ$C
4 to 105 $^\circ$C) in the range of 100 $^\circ$C to 125 $^\circ$C. The moisture
5 value is calculated as the loss in weight (difference
6 between the starting weight of sample and the final weight
7 of sample) divided by the starting weight of sample.
8 Similarly, a solids value can be calculated as the final
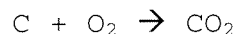9 weight of sample divided by the starting weight of sample.
10
11 **C.2.2 COMBUSTION STOICHIOMETRY**
12
13 Combustion stoichiometry calculations as described in
14 Section C.2.2 will be performed to aid in preparation for
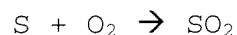15 combustion testing described in Section C.2.4
16
17 First, the weight percent values from Section C.2.1 are
18 converted to molar quantities on a dry basis.
19
20 Second, based on Chapter 3 of *Combustion Fundamentals for*
21 *Waste Incineration* (American Society of Mechanical
22 Engineers, 1974), the reaction products for these molar
23 quantities are calculated assuming complete combustion with
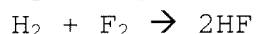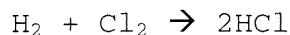24 the following rules:
25
26   a) All carbon (C) in feed converts to carbon dioxide (CO_2)
27         $C + O_2 \rightarrow CO_2$
28
29   b) All sulfur (S) in feed converts to sulfur dioxide (SO_2)
30         $S + O_2 \rightarrow SO_2$
31
32   c) The halogens (Cl, F) in feed convert to hydrogen halides
33         $H_2 + Cl_2 \rightarrow 2HCl$
34         $H_2 + F_2 \rightarrow 2HF$
35
36   d) Hydrogen (H) present in feed in excess of that
37   required to yield products in item c) above will be
38   converted to water
39         $2H_2 + O_2 \rightarrow 2H_2O$
40
41   e) Nitrogen (N) from feed or air is emitted as molecular
42   nitrogen
43         $N_2 \rightarrow N_2$
44
45 Third, with these rules, the balanced chemical reaction for
46 combustion of a compound can be written.
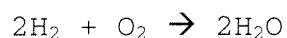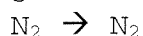
1 For example, the resulting reaction equation for a
2 hydrocarbon like methane (CH_4) is
3 $$CH_4 + 2\ O_2 \rightarrow CO_2 + 2H_2O$$
4
5 Note that the term feed in the preceding rules (a through
6 e) includes both material being combusted and the fuel
7 source of hydrogen such as methane or methanol.
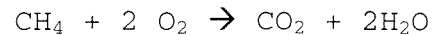8 Additionally, stoichiometric calculations as described
9 above presume that the compounds undergoing combustion are
10 essentially free of inorganic constituents.
11
12 These calculations provide the theoretical amount of oxygen
13 needed for the overall combustion reaction for the feed
14 based on the available information used in the
15 calculations. The initial estimate for the amount of
16 oxygen to be used in combustion testing will be determined
17 from this theoretical amount with adjustments for target
18 oxygen level in thermal reactor system exhaust gas. The
19 actual amount of oxygen to be used in combustion testing
20 will be based oxygen monitoring described in Section C.2.4.
21
22 These stoichiometric calculations will also be used as
23 needed to initially estimate and adjust experimental
24 conditions for combustion testing in Section C.2.4.
25
26 **C.2.3 THERMOGRAVIMETRIC ANALYSIS**
27
28 Thermogravimetric analysis (TGA) will be conducted to
29 determine the temperature range required for gasification
30 of each test substance composite. TGA will be conducted in
31 flowing air from room temperature to 1000°C as described in
32 Appendix B.1.
33
34 The TGA weight-loss profile for each test substance composite
35 will be evaluated to determine the temperature at which the
36 weight loss reaches a final asymptote across the temperature
37 range investigated. This temperature corresponds to the
38 point at which no further gasification (under test
39 conditions) occurs for the material and will be considered
40 the temperature for complete gasification of the material.
41
42 **C.2.4 Combustion Testing**
43
44 C.2.4.1 Test Objective
45
46 The objective of the testing program described in Appendix
47 C.2 is to assess the potential for waste incineration of

1   each test substance composite to emit PFOA, based on
2   quantitative determination of potential exhaust gas levels
3   of PFOA from laboratory-scale combustion testing under
4   conditions representative of typical municipal waste
5   combustor operations in the U.S.
6
7   C.2.4.2 Experimental Apparatus
8
9   Combustion testing will make use of the Advanced Thermal
10   Reactor System (ATRS) at the University of Dayton Research
11   Institute (UDRI). The ATRS is a laboratory-scale, non-
12   flame, batch-charged, continuous flow thermal reactor
13   system. The use of this non-flame thermal reactor system
14   gives a conservative representation of full-scale waste
15   incineration prior to air pollution controls.
16
17   In the ATRS, the test sample is gasified and transported to a
18   high temperature reactor. In the high temperature reactor,
19   the sample vapors are subjected to controlled conditions for
20   residence time and temperature. As described in Sections
21   C.2.4.5 and C.2.4.6, combustion products will be monitored or
22   collected for quantitative analysis.
23
24   A schematic of the ATRS as configured for this test program
25   is shown in Figure C.2-1.
26
27   **Figure C.2-1. Schematic of ATRS for this Test Program**

28
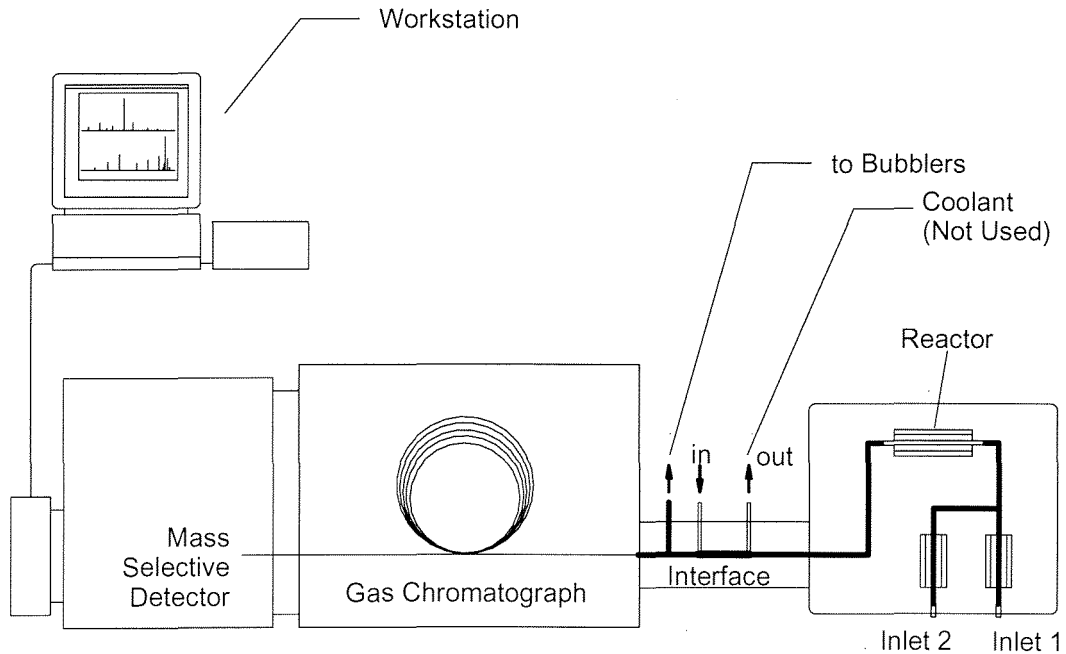
1   The ATRS consists of a reactor assembly and in-line gas
2   chromatograph/detector system connected via an interface.
3   The reactor assembly consists of a thermally insulated
4   enclosure housing the sample introduction, reactor, and
5   transfer line systems.
6
7   Sample introduction for solid materials (Inlet 1) employs a
8   pyroprobe, a device designed to gasify samples by heating
9   them at a fixed rate. The main gas flow will also be fed
10 via Inlet 1, and Inlet 2 will be used to feed supplemental
11 flow.
12
13 During combustion tests, the transfer line between the
14 pyroprobe and the reactor is heated and maintained above
15 200 °C. The reactor is housed within its own small tube
16 furnace and may be independently heated to as high as 1100
17 °C. (Actual conditions for this test program are presented
18 in Section C.2.4.3.) The transfer line from the reactor to
19 the interface is heat traced to greater than 200 °C to
20 prevent cool regions where reactor products could otherwise
21 be lost through condensation.
22
23 The interface routes the combustion exhaust gas to the in-
24 line gas chromatograph (GC) and mass selective detector
25 (MSD) or to sample collection for off-line analysis. For
26 combustion testing in this test program, the interface will
27 also be maintained above 200 °C. Exhaust gas monitoring for
28 this program is described in Section C.2.4.5.
29
30 C.2.4.3 Combustion Test Experimental Conditions
31
32 Each test substance composite will be subjected to
33 laboratory-scale incineration using the experimental
34 apparatus described in Section C.2.4.2.
35
36 C.2.4.3.1 Combustion Air
37
38 Synthetic air (mixture of 21% oxygen and 79% nitrogen) will
39 be used in place of compressed air to prevent potential
40 interference in the experimental system due to background
41 levels of CO_2 in compressed air.
42
43 C.2.4.3.2 Fuel
44
45 Methanol will be used, as needed, as a supplemental fuel to
46 ensure the presence of sufficient hydrogen to convert

1 fluorine to hydrogen fluoride (HF) and chlorine to hydrogen
2 chloride (HCl).
3
4 As noted in *Municipal Solid Waste in the United States:*
5 *2000 Facts and Figures* (EPA, 2002), paper and paper
6 products (made from wood) make up the largest component of
7 municipal solid waste (MSW). The sum of paper and paper
8 products with wood in MSW makes up over 30% of MSW.
9
10 During the 19th century, methanol was produced from wood and
11 was known as wood alcohol. Therefore, methanol can be used
12 in this experimental program as a surrogate for the paper
13 and wood fraction of MSW.
14
15 C.2.4.3.3 Operating Conditions
16
17 The target operating conditions for the high temperature
18 reactor during the combustion tests for each test substance
19 composite identified in Appendix A.3 are presented in Table
20 C.2-1.
21
22 **TABLE C.2-1. COMBUSTION TEST TARGET OPERATING CONDITIONS**

Temperature	1000 °C
Residence Time	2 sec
O_2 concentration in exhaust gas	10%
H_2O concentration in exhaust gas	15%
Number of replicate runs	3

23
24 These conditions are conservatively representative of
25 typical furnace operating conditions of municipal waste
26 combustors (MWCs) and of typical secondary chamber
27 operating temperatures for medical waste incinerators in
28 the U.S. See Appendix D.4 for supporting information.
29
30 Temperature and residence time values in Table C.2-2 will
31 be fixed setpoints for these experiments. The temperature
32 of the high temperature reactor will be controlled within
33 ± 10 °C to assure isothermal operation.
34
35 The amount of each test substance composite fed to the ATRS
36 in this testing program will be a measured amount less than
37 5 mg. The actual amount fed, gasification rate (determined
38 from TGA), air supply, and fuel supply will be adjusted to
39 assure that the oxygen level in the exhaust will be greater
40 than or equal to the concentration in Table C.2-1
41 throughout each test to be representative of typical MWC
42 conditions. The fuel supply and air supply will also be

1 adjusted as needed to approach the target H_2O concentration
2 in exhaust gas in Table C.2-1.
3
4 The pyroprobe section final temperature (at end of
5 temperature ramp-up) will be 750 °C or as needed to assure
6 this section is 50 to 100 °C above the highest temperature
7 for complete gasification across the test substance
8 composites as determined from the TGA results; see Section
9 C.2.3. This is necessary to assure complete gasification
10 of the sample of test substance composite and a common set
11 of experimental conditions across the test materials during
12 combustion testing.
13
14 C.2.4.3.4 Blanks
15
16 A minimum of one thermal blank will be run prior to each
17 set of three combustion test runs for a given test
18 substance composite. Each thermal blank run will be at the
19 corresponding combustion test conditions with all feeds
20 except for the test substance.
21
22 C.2.4.4 Process Monitoring
23
24 ATRS process parameters in Table C.2-2 will be monitored
25 for each combustion test at key points during the test as
26 noted in the table. Each combustion test will be a minimum
27 of 5 minutes in duration. If the duration of a combustion
28 test is greater than 15 minutes, each parameter in Table
29 C.2-2 will be recorded at least once every 15 minutes.
30
31 **TABLE C.2-2. COMBUSTION TEST MONITORING**

Parameter	Key Time for Recording
Temperature-Reactor	Before & after gasification
Temperature-Transfer line	Before & after gasification
Temperature-Inlet 1	After gasification
Temperature-Inlet 2	Before & after gasification
Gas flow rate-Inlet 1	Before & after gasification
Gas flow rate-Inlet 2	Before & after gasification
Total Gas Flow rate	Before & after combustion test
Make-up Gas (He) Flow rate	Before & after combustion test
Pressure-Reactor	Before & after gasification

32
33 Temperature-Inlet 1 will be recorded at the end of the
34 temperature ramp-up for gasification to monitor the
35 pyroprobe final temperature.
36

1 The flow rate of the exhaust gas routed to the bubblers
2 (see Section C.2.4.5.2) will be determined based on the
3 flow measurements listed in Table C.2-2.
4
5 The amount of material fed to the system will be verified
6 by weighing the pyroprobe insert cartridge before and after
7 each experiment.
8
9 Exhaust gas monitoring is described in Section C.2.4.5.
10
11 C.2.4.5   Exhaust Gas Monitoring
12
13 Combustion exhaust gas will be continuously monitored for
14 oxygen during each combustion test via in-line MSD or via
15 an oxygen monitor. CO_2 in exhaust gas will be monitored via
16 in-line GC, in-line MSD, or a continuous monitor; or
17 exhaust gas will be collected in Tedlar® bags for off-line
18 analysis of CO_2. Carbon monoxide (CO) in exhaust gas will
19 be monitored via in-line GC or a continuous monitor; or
20 exhaust gas will be collected in Tedlar® bags for off-line
21 analysis of CO. Tedlar® bag samples may be collected at
22 the exit of the bubblers described in Section C.2.4.6.
23
24 C.2.4.6 Exhaust Gas Sampling
25
26 Gas samples for off-line analysis will be collected as
27 described in Appendix D.1, revised as necessary pursuant to
28 Appendix C.1.2.2 if applicable.
29
30 A minimum of 60 mL of bubbler aqueous solution composite is
31 expected from each combustion test. Of this, a minimum of
32 45 mL will be directed to PFOA analysis, and the remainder
33 will be directed to fluoride ion analysis.
34
35 C.2.4.7 Exhaust Gas Analysis
36
37 C.2.4.7.1 Fluoride Ion
38
39 A portion of the composite bubbler aqueous solution sample
40 from each combustion test collected as described in Section
41 C.2.4.6 will be analyzed for fluoride ion via ion
42 chromatography using EPA Method 300.0.
43
44 C.2.4.7.2 PFOA
45
46 A portion of the composite bubbler aqueous solution sample
47 from each combustion test collected as described in Section

1   C.2.4.6 will be analyzed for PFOA via LC/MS/MS as described
2   in Appendix D.2.
3
4   As described in Appendix D.2, composite bubbler aqueous
5   solution sample results less than method detection limit
6   (MDL) will be reported as not detected (ND), results
7   between MDL and the limit of quantitation (LOQ) will be
8   reported as not quantifiable (NQ), and numerical values
9   will not be reported.
10
11 Due to background levels of PFOA, the analytical laboratory
12 will only report numerical values for PFOA concentration in
13 the aqueous solution greater than or equal to the LOQ.
14 This is required to assure that the reported concentration
15 value is attributable to the aqueous solution sample rather
16 than to background.
17
18 C.2.5 Reporting of Results
19
20 C.2.5.1 Elemental Analysis Results
21
22 The results of elemental analysis for each test substance
23 composite (as noted in Section C.2.1) will be reported.
24 The laboratory reports will be included in an appendix to
25 the final report for incineration testing (test report).
26
27 C.2.5.2 Combustion Stoichiometry Results
28
29 Combustion stoichiometry (as noted in Section C.2.2)
30 calculations for each test substance composite will be
31 included in an appendix to the test report.
32
33 C.2.5.3 TGA Results
34
35 The temperature for complete gasification and the TGA
36 graphical results for each test substance composite (as
37 noted in Section C.2.3) will be included in an appendix to
38 the test report.
39
40 C.2.5.4   Combustion Test Results
41
42 C.2.5.4.1 Process Monitoring
43
44 Process monitoring data (as noted in Section C.2.4.4)
45 recorded for each combustion test will be reported in
46 tabular form.
47

C.2.5.4.2 Exhaust Gas Monitoring

Exhaust gas O_2, CO and CO_2 monitoring results will be reported as the integrated or average value for each combustion test. CO will be reported in terms of parts per million by volume (ppmv). O_2 and CO_2 will be reported in terms of percent by volume (%).

C.2.5.4.3 Exhaust Gas Analytical Results

Results of analyses noted in Section C.2.4.7 will be reported for each replicate of each combustion test.

The analytical result for each analyte in Section C.2.4.7 will be reported in terms of concentration (mass per volume) in the bubbler aqueous solution. For each analyte, this value will be used with the associated exhaust gas volume to compute an exhaust gas concentration and with the associated test substance mass to compute mass of analyte per mass of test substance composite.

C.2.5.4.3.1 Fluoride

Fluoride ion in the exhaust gas will be reported on the basis of mass of fluoride ion per mass of test substance composite. The corresponding hydrogen fluoride value for each will also be computed and reported for reference.

C.2.5.4.3.2 PFOA

PFOA results for the bubbler aqueous solution samples will be reported as described in Section C.2.4.7.2. PFOA results for associated blanks will also be reported.

If present in the bubbler aqueous solution at a concentration above the matrix-specific LOQ, PFOA in the exhaust gas will be reported on the basis of mass of PFOA per mass of test substance composite.

C.2.5.5 Release Assessment

In the event that PFOA is reported for the exhaust gas bubbler aqueous solution at a concentration at or above the LOQ (as defined in Appendix D.2) for two or more of the three runs for a given test substance composite, a release assessment report for the full-scale waste incineration of products represented by the test substance composite will

1 be prepared following the outline in Appendix E.2 and will
2 be included in the test report.
3
4 C.2.5.6 Test Report Outline
5
6 The outline for the test report is presented in Appendix
7 E.3. All reporting discussed in Sections C.2.5.1 through
8 C.2.5.5 will be included in this test report, as
9 applicable.

1 **APPENDIX D.1**
2 **EXHAUST GAS SAMPLING VIA BUBBLERS**
3
4 Gas samples for off-line analysis will be collected from a
5 vent line off the interface of the thermal reactor system
6 described in Appendix C.2.4. Flexible (silicone or
7 equivalent) tubing will connect the vent line and a set of
8 bubblers.
9
10 Gas absorption via these bubblers will provide aqueous
11 solution (of documented content) to analyze for prescribed
12 parameters. Two to four bubblers (low pressure drop
13 impingers) in series will be used. Each bubbler will
14 contain a predetermined amount of aqueous solution, and the
15 total amount of solution at the beginning of each test run
16 will be a minimum of 55 mL. The temperature of the gas
17 exiting the last bubbler will be monitored.
18
19 An additional bubbler (which is empty) will be added to the
20 front end of this series of bubblers to serve as a knock-
21 out pot if calculations or preliminary measurements
22 indicate that greater than 10 mL of water will be produced
23 during the testing for a given material.
24
25 Upon completion of sample collection, the amount in each
26 bubbler will be weighed and recorded, and the contents of
27 the bubblers will be composited for subsequent analysis.
28 Additionally, the flexible tubing will be rinsed with 5 mL
29 of HPLC water to collect potential condensate in the
30 tubing; this rinsate will be combined with the bubbler
31 composite prior to analysis.
32
33 Bubbler aqueous solution composites will be conveyed to
34 analytical laboratory(ies) in polyethylene, polypropylene,
35 or glass container(s).

1 **APPENDIX D.2**
2 **PFOA ANALYSIS BY LC/MS/MS**
3
4 D.2.1 Introduction
5
6 Samples to be analyzed for PFOA in this study will be
7 subjected to Liquid Chromatography with Tandem Mass
8 Spectrometry (LC/MS/MS) in accordance with "Method of
9 Analysis for the Determination of Ammonium
10 Perfluorooctanoate (APFO) in Water Revision 1" (Exygen
11 method) revised per the section-by-section comments listed
12 in Section D.2.4 below. These revisions are necessary to
13 adapt a method originally developed for liter quantity
14 water samples to samples related to testing described in
15 Appendix C.
16
17 The testing programs described in Appendix C are expected
18 to generate samples of aqueous solution, methanol (e.g., as
19 used for extraction or rinsing), and corresponding blanks.
20 The expected sample size for aqueous solution samples (from
21 exhaust gas bubbler sample collection) available for
22 analysis via this method is approximately 50 mL.
23
24 D.2.2 Method Summary
25
26 PFOA is extracted from water using a disposable C_{18} solid
27 phase extraction (SPE) cartridge. PFOA is eluted from the
28 cartridge with methanol. Quantification of PFOA is
29 accomplished by electrospray liquid chromatography/tandem
30 mass spectrometry (LC/MS/MS) analysis.
31
32 D.2.3 Reporting
33
34 The target limit of quantitation (LOQ) for this study with
35 this method is 50 ng/L based on prior work with water
36 samples where an 8-fold concentration via extraction using
37 C_{18} SPE cartridge has been demonstrated. The actual LOQ
38 will be matrix dependent; for samples (e.g., methanol
39 rinsate) where the 8-fold concentration cannot be
40 performed, the target LOQ for this study is 400 ng/L.
41
42 Sections 4.5.4 and 5 of the Exygen method explain reporting
43 for field samples such as bubbler aqueous solution
44 composites, which are distinct from blanks and spikes, as
45 follows:
46
47   Field samples in which either no peaks or peaks

1   less than the MDL are detected at the corresponding
2   analyte retention time will be reported as ND (not
3   detected). Samples in which peaks are detected at
4   the corresponding analyte retention time that are
5   less than the LOQ and greater than or equal to the
6   MDL will be reported as NQ (not quantifiable).
7
8 Therefore, sample results less than method detection limit
9 (MDL) will be reported as ND, and sample results between
10 MDL and the limit of quantitation (LOQ) will be reported as
11 NQ. Numerical values will not be reported for such
12 samples. Only concentrations above the LOQ, where the
13 reported concentration is attributable to the sample rather
14 than to background, are reported with numerical values.
15
16 Additionally, if the PFOA anion is found in a sample at a
17 concentration above the LOQ for the matrix but is less than
18 5 times the concentration found in the associated blank,
19 the result will be reported, flagged, and treated as ND.
20
21 D.2.4 Study-Specific Comments on the Method
22

Section	Comment
1	• The concentration of PFOA found will be reported directly and the mathematical conversion for reporting as APFO mentioned in the 4th sentence of the 2nd paragraph will not be performed. • Since the 8-fold concentration described in the 2nd sentence 4th paragraph (which forms the basis for the LOQ in the 3rd paragraph and the MDL in the 4th paragraph) is dependent on having a minimum of 40 mL of aqueous sample amenable to extraction using the C_{18} SPE cartridge described in section 4.4 of the method, the LOQ and MDL in the method will be a factor of 8 higher than reported where less than 40 mL of sample is available or where the sample is not amenable to extraction using the C_{18} SPE cartridge described in section 4.4 of the method (e.g., methanol).
3.3 Note at top of page 8	• The note stating "Equivalent materials may be substituted for those specified in this method if they can be shown to produce satisfactory results" will not be used in the analysis for this testing program.

3.3 Notes, Note 1	• The following text will be used in place of Note 1 with respect to the PFOA analysis conducted for this testing program: In order to avoid contamination, the use of disposable labware (tubes, pipets, etc.) is required.
3.3 Notes, Note 4	• The following text will be used in place of Note 4 with respect to the PFOA analysis conducted for this testing program: Solvents (e.g., methanol) used for this analysis must be checked for the presence of contaminants by LC/MS/MS before use.
3.5 opening text prior to 3.5.1	• Where the available amount of sample is expected to be much less than 1 liter, insufficient sample is available to prepare the fortified matrix spikes described in the opening text of section 3.5. In this case, the analytical standards discussed in this opening text will be limited to two purposes since the third purpose (matrix spike) stated in the method cannot be done.
4.3, item b	• Where the available amount of sample is expected to be less than 80 mL (= 2 * 40), the replicate extraction noted in the first sentence of this item cannot be performed. • If the sample is not an aqueous sample amenable to extraction using the C_{18} SPE cartridge described in section 4.4 of the method, then section 4.4 is skipped such that the sample is analyzed directly. (Note: For such samples, the LOQ and MDL will be 8 times higher than the values quoted in the method.)
4.3, item c	• As noted in comment on section 3.5 opening text above, fortified matrix spikes will not be prepared when the available amount of sample is much less than 1 liter. • Where the available amount of sample is expected to be less than 80 mL (= 2 * 40), the conditional repeat fortification and extraction described in the third sentence of this item cannot be performed.
4.4	• Extraction using the C_{18} SPE cartridge requires a suitable aqueous sample. This extraction and the corresponding 8-fold concentration

	pointed out in the NOTE at the end of this section cannot be performed on non-aqueous (e.g., methanol) samples.
4.4, item 1	• In order to measure out the 40 mL mentioned in this item, it is necessary to have at least 45 mL of sample to enable pipet transfer.
4.5.4, item g	• A storage stability study for PFOA in water performed independently of the development of the method indicates that PFOA may be stored in glass, polystyrene, polypropylene, or polyethylene containers without measurable degradation for up to 68 days prior to extraction. Therefore, the total holding time between sample collection and analysis for aqueous PFOA samples in this study may exceed the 14 day limit noted in the first sentence of this item provided that the sample is not held for greater than 68 days unless additional storage stability testing justifies a longer hold time.
4.6, item 3	• As noted in comment on section 3.5 opening text above, fortified matrix spikes will not be prepared when the available amount of sample is much less than 1 liter. In this case, acceptance criteria for matrix spike recoveries will not be considered.
5, item c	• The calculation in equation 3 in this section will not be performed since it is not necessary to convert the PFOA analytical results to APFO for this study.

1
2   D.2.5 Reference
3
4   Flaherty, J. and K. Risha, "Method of Analysis for the
5   Determination of Ammonium Perfluorooctanoate (APFO) in
6   Water Revision 1", Exygen Method No. 01M-008-046 Revision
7   1, January 2003. (EPA Docket ID OPPT-2003-0012-0040)

1 **APPENDIX D.3**
2 **WICKBOLD TORCH METHOD FOR TOTAL FLUORINE**
3
4 D.3.1 Introduction
5
6 "The carbon-fluorine bond is exceptionally strong, and
7 extremely vigorous conditions are needed for quantitative"
8 analysis of fluorine in organic compounds. (Kissa, 1998)
9 The "most vigorous" technique for measurement of fluorine
10 in organic compounds is "combustion in an oxyhydrogen
11 flame" referred to as the Wickbold torch. (Kissa, 1998)
12
13 D.3.2 Apparatus
14
15 A typical configuration for the Wickbold oxyhydrogen torch
16 apparatus as described by Sweetser (1956) is shown in
17 Figure D.3-1.
18
19
20 **FIGURE D.3-1.   WICKBOLD OXYHYDROGEN TORCH APPARATUS**
21
22
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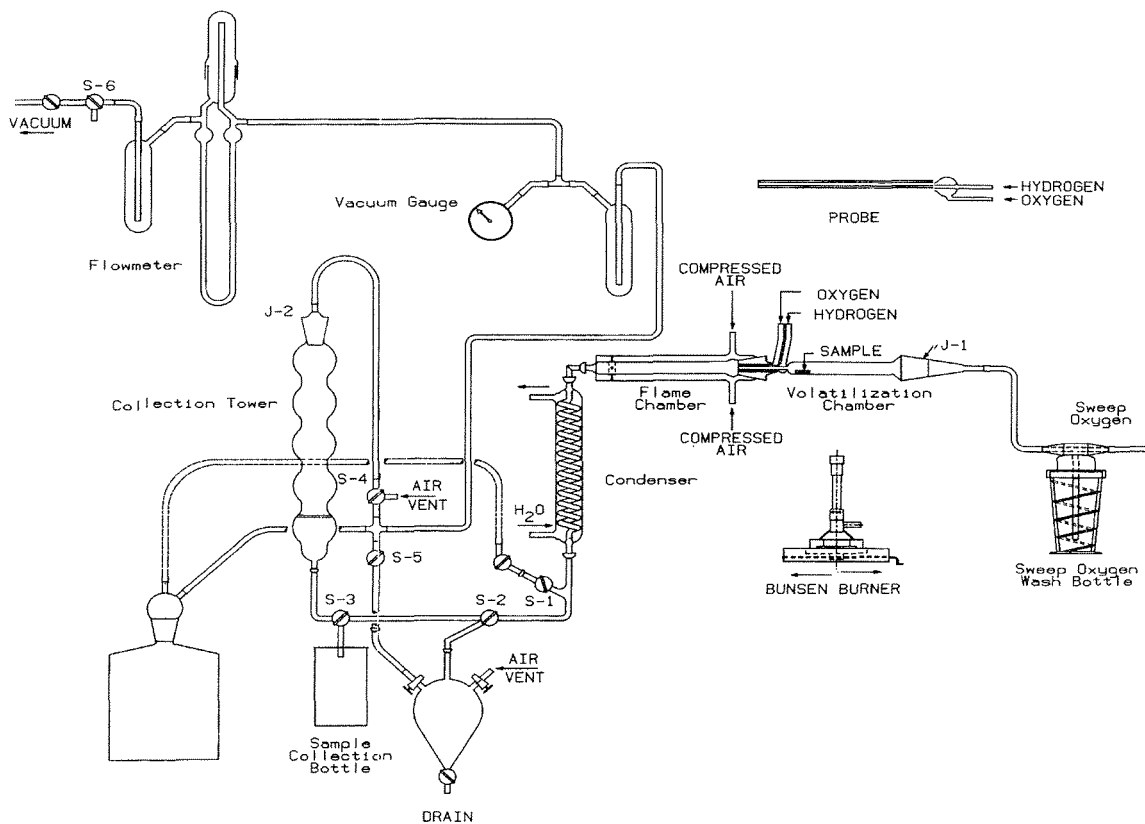
D.3.3 Method Description

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

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

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

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

D.3.4 Safety Considerations

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

D.3.5 References

Kissa, E. "Analysis of Anionic Fluorinated Surfactants", Chapter 8 in Anionic Surfactants: Analytical Chemistry – 2nd Edition, Revised and Expanded, edited by John Cross. Marcel Dekker Surfactant Science Series, volume 73, 1998.

Sweetser, P. B. "Decomposition of Organic Fluorine Compounds by Wickbold Oxyhydrogen Flame Combustion Method", Analytical Chemistry, vol. 28, pp. 1766-1768, 1956.

1 **APENDIX D.4**
2 **WASTE INCINERATION AND OPERATION CONDITIONS**
3
4 Polymers of the sort being investigated in this testing
5 program may be present at trace to low concentrations in
6 the feedstreams to municipal waste combustors and/or
7 medical waste incinerators in the U.S.
8
9 **D.4.1 Types of Incinerators**
10
11 D.4.2.1 Municipal Waste Combustors
12
13 According to the Integrated Waste Services Association
14 (IWSA), there are a total of 98 waste-to-energy facilities
15 operating municipal waste combustors (MWCs) in the U.S. as
16 of 2002. (IWSA 2002) Table D.4-1 summarizes the number and
17 annual capacity of these units by type of technology
18 employed.
19
20 **Table D.4-1. MWCs in 2002**

Type	Number of Facilities	Annual Capacity (million Ton/year)	Fraction of Waste
Mass Burn	68	22.5	76.5%
Refused Derived Fuel (RDF)	18	6.4	21.8%
Modular	12	0.5	1.7%
Total	98	29.4	100.0%

21
22 D.4.1.2 Hospital/Medical/Infectious Waste Incinerators
23
24 Although earlier reports indicated approximately 2400
25 medical waste incinerators in the U.S. in the 1990s burning
26 approximately 846 thousand tons of hospital and
27 medical/infectious waste (EPA 1997), the current EPA Office
28 of Air Quality, Planning, and Standards (OAQPS) inventory
29 indicates that there are 116 hospital/medical/infectious
30 waste incinerators (HMIWIs) in the U.S. as of July 28,
31 2003. (EPA 2003)
32
33 This represents a greater than 90% reduction in the number
34 of operating HMIWIs in the U.S. Many medical waste
35 incinerators were closed rather than upgraded to meet new
36 emission standards, as hospitals improved their programs to
37 segregate infectious ("red bag") waste burned in HMIWIs
38 from non-infectious ("black bag") waste handled as
39 municipal solid waste after it leaves the hospital.
40 Consequently, the amount of segregated infectious waste

1 burned in HMIWIs is expected to be less than 0.3 million
2 tons per year.
3
4 EPA notes that over 97% of medical waste incinerators are
5 controlled air modular units (EPA 2000a). Recent
6 communication with EPA OAQPS indicates that virtually all
7 existing HMIWIs are controlled air modular (two-chamber)
8 units.
9
10 **D.4.2 Incinerator Operating Conditions**
11
12 Many incinerators for municipal solid waste are designed to
13 operate in the combustion zone at 1800 °F (982 °C) to 2000
14 °F (1093 °C) to ensure good combustion. (EPA 1995) EPA's
15 new source performance standards (NSPS) and emission
16 guidelines for both municipal waste combustors (MWCs) and
17 hospital/medical/infectious waste incinerators (HMIWIs) are
18 based on the use of "good combustion practices" (GCP). (EPA
19 1997, EPA 2000b, EPA 2000c, Van Remmen 1998)
20
21 Referring to MWCs, Donnelly notes, "Design of modern
22 efficient combustors is such that there is adequate
23 turbulence in the flue gas to ensure good mixing, a high-
24 temperature zone (greater than 1000 °C) to complete burnout,
25 and long enough residence time at high temperature (1-2
26 sec) for complete burnout." (Donnelly 2000) The term "flue
27 gas" here refers to the gas above the grate.
28
29 With respect to HMIWIs, Van Remmen states "any unit which
30 presently [prior to compliance date] has a [secondary
31 chamber] residence time less than two seconds at 1000 °C
32 does not meet the requirement for good combustion under the
33 new regulations." (Van Remmen 1998)
34
35 Similarly, most MWCs operate with a 2 second gas residence
36 time in the high temperature zone in order to assure
37 compliance with emission standards on carbon monoxide (CO)
38 and dioxins.
39
40 D.4.2.1 MWC Operating Conditions
41
42 D.4.2.1.1 Mass Burn MWC
43
44 Review of the IWSA Directory (IWSA 2002) indicates that
45 almost all of these mass burn units are mass burn water
46 wall furnaces.   Nearly all mass burn water wall furnaces

 1   have reciprocating grates or roller grates to move the
 2   waste through the combustion chamber. (EPA 1996a)
 3
 4   Studies on the Millbury, Massachusetts mass burn water wall
 5   MWC produced gas temperature versus residence time results.
 6   (Scavuzzo, Strempek, and Strach 1990) Calculations based
 7   on Figure 6 of this paper indicate a time-averaged
 8   temperature of 2238 °F (1226 °C) over a 2 second. The
 9   corresponding gas temeperature at the 2 second level from
10   this figure is 1750 °F (954 °C).
11
12   A report on the Warren County, New Jersey mass burn water
13   wall MWC indicates that the design gas temperature between
14   the grate and secondary air inject was greater than 2000 °F
15   (1093 °C) over a gas residence time of an additional 2.2
16   seconds. (Schuetzenduebel and Nobles 1990) This report
17   also shows that this MWC was designed for 2 seconds
18   residence time above 1800 °F (982 °C) between the
19   introduction of secondary air and the exit of the furnace
20   section. (Schuetzenduebel and Nobles 1990) The temperature
21   profile (Figure 21) in the temperature correlation test
22   report (Schutzenduebel 1989) for this MWC shows the full
23   load gas temperature at the secondary air injection point
24   is 2650 °F, and the gas temperature at the 2-second point is
25   1850 °F. Therefore, testing indicates an average
26   temperature of 2250 °F (1232 °C) over this 2 second gas
27   residence time for the Warren County unit. A related
28   report for the Warren County MWC by the design firm
29   indicates that the exhaust gas oxygen concentration is
30   nominally 10% (dry basis). (Blount Energy Resource Corp.
31   1989)
32
33   Information from these 2 MWCs demonstrates that the average
34   gas temperature across a 2 second residence time for mass
35   burn MWCs is conservatively expected to be greater than
36   1100 °C.
37
38   Test report data from a typical mass burn MWC (Fairfax,
39   Virginia) indicates typical average furnace exit gas
40   concentrations are 10.8% oxygen (dry basis) and 18.4%
41   moisture (water). (Clean Air Engineering, 1997)
42
43   As indicated in Table D.4.1, mass burn units account for
44   over 76% of the municipal solid waste incinerated in the
45   U.S.

1
2 D.4.2.1.2 RDF MWC
3
4 Furnace temperatures as well as flue gas oxygen and moisture
5 (H_2O) levels for the Mid-Connecticut RDF combustor during
6 performance tests while operating under good combustion
7 conditions across a range of steam loads (Finklestein and
8 Klicius 1994) are summarized in Table D.4-2.
9
10 **Table D.4-2. RDF MWC – Mid-Connecticut**

Steam load	low	low	inter-mediate	inter-mediate	normal	normal	normal	high
test number	PT-13	PT-14	PT-10	PT-02	PT-09	PT-08	PT-11	PT-12
Furnace temperature (°C)	965	1004	1012	1022	1033	1015	1026	1049
flue gas O_2 (%)	10.1	9.6	9.2	9.1	7.6	7.5	7.9	6.4
flue gas moisture	12.4	11.1	12.3	15.4	15.1	16.3	14.1	16.2

11
12 The average operating conditions for this RDF unit across
13 the range of steam loads are 1016 °C, 8.4% O_2 (dry basis),
14 and 14.1% moisture.
15
16 Examination of the report and MWC temperature monitoring
17 practices indicates that these temperatures are effectively
18 combustion zone exit temperatures. Therefore, in order to
19 determine the average MWC combustion zone temperature
20 across a 2 second gas residence time, it is necessary to
21 understand the time-temperature profile of the MWC.
22
23 Since waste combustion in this and most other RDF units in
24 the U.S. involves burning on the grate (EPA 1996a) similar
25 to the operation of mass burn MWCs, the time-temperature
26 profile in an RDF unit is expected to be similar to that
27 described in Section D.4.2.1.1 above. Based on this
28 similarity and the temperatures in Table D.4-2, the average
29 gas temperature across a 2 second residence time for RDF
30 units is conservatively expected to be greater than 1100 °C.
31
32 As indicated in Table D.4.1, RDF units account for
33 approximately 22% of the municipal solid waste incinerated
34 in the U.S.
35
36 D.4.2.1.1 Modular MWC
37
38 Modular MWCs are generally small dual-chamber units,
39 accounting for less than a total of 2% of the municipal
40 solid waste incinerated in the U.S. in 2002. Modular MWCs
41 are generally equipped with auxiliary fuel burners in the

1 secondary chamber. (EPA 1996a) EPA notes that the
2 secondary chamber exit temperature of modular MWCs is
3 maintained at typically 980 to 1200 °C. (EPA 1996a)
4
5 A typical modular MWC in Polk County, Minnesota is operated
6 with a gas residence time of 2 seconds, in the secondary
7 chamber, a secondary chamber exit temperature in the range
8 of 1800 °F (982 °C) to 2000 °F (1093 °C), flue gas oxygen
9 concentrations in the range of 10% to 13% (dry basis), and
10 flue gas moisture in the range of 10% to 15% (Pace
11 Analytical 2003).
12
13 Since the secondary chamber exit temperature is expected to
14 be the minimum gas-phase temperature for the chamber, the
15 secondary chamber average gas temperatures for modular MWCs
16 are expected to be 1000 °C or greater.
17
18 As indicated in section D.4.1, such modular units are
19 generally small MWCs and account for less than a total of
20 2% of the municipal solid waste incinerated in the U.S.
21
22 D.4.2.1.4 MWC Summary
23
24 Considering the relative quantities of municipal waste
25 burned annually in each type of MWC and the data in this
26 section, typical operating conditions for the high
27 temperature zone of most MWCs are >1000 °C average
28 temperature across 2 second residence time with exit gas
29 concentrations of 10% O_2 (dry basis) and >15% moisture.
30
31 D.4.2.2 HMIWI Operating Conditions
32
33 The range of temperatures for the secondary chamber of
34 controlled air medical waste incinerators has been reported
35 as 980 to 1200 °C. (Theodore 1990) EPA notes that auxiliary
36 fuel (e.g., natural gas) is burned in the secondary chamber
37 of medical waste incinerators to sustain temperatures in
38 the range of 985 to 1095 °C and that combustion air at 150
39 to 250 % of the stoichiometric requirement is usually added
40 to the secondary chamber. (EPA 2000a, EPA 1994a)
41
42 In its model plant description background document, EPA
43 notes that the average moisture content in HMIWI flue gas
44 was about 10 % based on available data, and EPA states
45 "limited data show that older [HMIWI] units typically have
46 residence times that range from essentially 0 seconds up to
47 about 1 second." (EPA 1994b) However, as noted above, a

1 more recent report indicates that HMIWIs still in operation
2 have secondary chamber temperatures greater than or equal
3 to 1000 °C with a gas residence time of 2 seconds. (Van
4 Remmen 1998) For example, EPA studied the incinerator at
5 Weeks Hospital in New Hampshire as a typical HMIWI with a
6 design residence time of 2 seconds in the secondary
7 chamber. (EPA 1996b) During this testing, the average exit
8 secondary chamber exit temperature was 1024 °C, and the flue
9 gas oxygen concentration was 13.5%. (dry basis)(EPA 1996b)
10
11 Review of test reports for all HMIWIs in the EPA docket for
12 the HMIWI NSPS and EG rulemakings that are listed in EPA's
13 current HMIWI inventory (EPA 2003) does not refute Van
14 Remmen's statement above on residence time and temperature
15 and indicates HMIWI flue gas oxygen concentrations for
16 these units in the range of 10 to 15% (dry basis)and stack
17 moisture concentrations as high as 30% (after wet
18 scrubbing).   (Environmental Laboratories Inc. 1993, EPA
19 1996, HDR Engineering 1994a, HDR Engineering 1994b, METCO
20 Environmental 1992, Technical Services, Inc. 1993,
21 Technical Services, Inc. 1994a, Technical Services, Inc.
22 1994b) Apparently, the older HMIWIs referred to in EPA's
23 model plant description background document either have
24 been shut down or upgraded to operate with secondary
25 chamber exit temperatures higher than 1000 °C at a gas
26 residence time of 2 seconds.
27
28 Secondary chamber temperature of HMIWIs is monitored near
29 the secondary chamber outlet. (EPA 1994) Hence, when the
30 auxiliary burner (located on the end opposite from the
31 outlet) is in use, the average gas temperature in an HMIWI
32 secondary chamber is greater than the outlet temperatures
33 noted above. Therefore, secondary chamber average gas
34 temperatures for HMIWIs are expected to be 1000 °C or
35 greater with a gas residence time of 2 seconds.
36
37 In summary, typical operating conditions for the secondary
38 chamber of operating HMIWIs in the U.S. are 1000 °C average
39 temperature across 2 second residence time with exit gas
40 concentrations of 13% O_2 (dry basis) and >10% moisture.
41
42 **D.4.3 Pollution Control Equipment**
43
44 Over 99% of large MWC capacity operates with a spray dryer
45 absorber/scrubber. (IWSA 2003) Approximately 80% of large
46 MWC capacity operates using carbon injection as part of the
47 pollution control system. (IWSA 2003) Due to requirements

1 in the NSPS (EPA 2000b) and EG (EPA 200c) for small MWCs,
2 small MWCs planning continued operation are generally
3 upgrading or have upgraded their pollution control
4 equipment to add spray dryer absorbers or other acid gas
5 control and carbon injection.
6
7 Review of EPA's HMIWI inventory (EPA 2003) indicates that
8 essentially all HMIWIs have some form of wet or dry
9 scrubbing for acid gas control.
10
11 **D.4.4 Summary**
12
13 Approximately 30 million tons per year of municipal solid
14 waste was combusted in the United States annually in waste-
15 to-energy municipal waste combustors in 2003.
16 Approximately 0.3 million tons per year of segregated
17 medical waste was combusted annually in the United States
18 in hospital/medical/infectious waste incinerators in 2003.
19 Considering the relative amounts of waste combusted
20 annually, typical operating conditions for waste
21 incineration in the U.S. across these two classes of units
22 are as follows:
23

Average Temperature	>1000 °C
Residence Time	>2 sec
O_2 concentration in exhaust gas	10% (dry basis)
H_2O concentration in exhaust gas	15%

24
25 EPA emission regulations currently in place or in place by
26 2005 require that operating municipal waste combustors and
27 hospital/medical/infectious waste incinerators have or will
28 have air pollution control equipment such as wet or dry
29 scrubbing for acid gas control.
30

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1 **APPENDIX E.1** (Fluorotelomers)
2 **OUTLINE FOR INTERIM PROGRESS REPORTING**
3
4
5 Title: Enforceable Consent Agreement for the Laboratory-
6   Scale Incineration Testing of Fluorotelomer Based
7   Polymers - Interim Report
8
9 OPPT Docket ID No: OPPT-2004-0001
10
11 Date of Interim Report: [date   ]
12
13
14
15 This Report covers the period from [date] to [date]
16
17
18 1)   List or description of significant ECA Test Program
19   milestones during this period:
20
21
22
23
24
25 2)   Description of Difficulties: (If none indicate N/A)
26
27
28
29
30
31
32
33 3)   Actions taken in response to difficulties: If none
34   indicate N/A)
35
36
37
38
39
40
41 4)   Other information relevant to the progress of the
42   testing program: (If none indicate N/A)
43

1 **APPENDIX E.1** (Fluoropolymers)
2 **OUTLINE FOR INTERIM PROGRESS REPORTING**
3
4
5 Title: Enforceable Consent Agreement for the Laboratory-
6   Scale Incineration Testing of Fluoropolymers –
7   Interim Report
8
9 OPPT Docket ID No: OPPT-2003-0071
10
11 Date of Interim Report: [date   ]
12
13
14
15 This Report covers the period from [date] to [date]
16
17
18 1)   List or description of significant ECA Test Program
19   milestones during this period:
20
21
22
23
24
25 2)   Description of Difficulties: (If none indicate N/A)
26
27
28
29
30
31
32
33 3)   Actions taken in response to difficulties: If none
34   indicate N/A)
35
36
37
38
39
40
41 4)   Other information relevant to the progress of the
42   testing program: (If none indicate N/A)

1   **APPENDIX E.2**
2   **OUTLINE FOR RELEASE ASSESSMENT REPORT**
3
4   As described in Appendix C.2.5.5 of this ECA, if PFOA is
5   reported for the exhaust gas bubbler aqueous solution at a
6   concentration at or above the LOQ (as defined in Appendix
7   D.2) for two or more of the three runs for a given test
8   substance composite, then the potential for release from
9   full-scale municipal and/or medical waste incineration, as
10 applicable, (including application of air pollution
11 controls) of products represented by the test substance
12 composite in the United States will be assessed to put the
13 data into perspective. At a minimum, the report will
14 follow the general outline described below and will state
15 assumptions, document the basis for the assumptions made,
16 quantitatively estimate the variability of calculated
17 estimates (based on the variability of the parameters in
18 the evaluation), and qualitatively discuss the uncertainty
19 of calculated estimates.
20
21 **1.0   Introduction**
22
23   • Statement of objective for combustion testing of
24   test substance composites.
25
26   • Applicability of the laboratory-scale combustion
27   testing to full-scale municipal waste combustors
28   (MWCs) and/or medical waste incinerators (as
29   applicable) in the United States.
30
31 **2.0   Summary of study results**
32
33   • A listing of exhaust gas analytical results reported
34   for each applicable test substance composite.
35
36   • A listing of test substance composite analytical
37   results reported for each applicable test substance
38   composite.
39
40 **3.0   Discussion**
41
42   • Description of the combustion section of the
43   applicable waste incineration process(es) being
44   evaluated (MWC and/or medical waste incinerator)
45   including the rationale for selecting test target
46   temperature(s) and description of typical

1   operational parameters. Cross-reference to or
2   submission of relevant parts of Appendix D.4 of this
3   ECA can satisfy this provision.
4

5   • Description of the post-combustion air pollution
6   control equipment (e.g., lime scrubbing, carbon
7   adsorption) employed by typical operating full-scale
8   waste incineration process(es) as applicable.
9

10 4.0 Extrapolation of laboratory test results to the
11   typical waste incineration process(es), as applicable,
12   described in Section 3.0 (above) for each test
13   substance composite to be evaluated.
14

15   • The relevance of the subject test substance
16   composite to MWCs and/or medical waste incinerators.
17

18   • The estimated concentration of the subject test
19   substance composite to the applicable type(s) of
20   waste incinerator. Available information on
21   hydrogen fluoride concentration in waste incinerator
22   exhaust can provide the basis for an upper bound on
23   this estimated concentration.
24

25   • A description of the extrapolation.
26

27   • A description of any assumptions used.
28

29   • Any unique qualitative or quantitative descriptors
30   of the test, the testing equipment, and the results
31   deemed necessary for informative review of the test
32   and test results.
33

34 5.0 Sensitivity Analysis
35

36   • Assessment of the impact of variability
37   (quantitative) and uncertainty (qualitative) in each
38   parameter on the evaluation results.
39

40 6.0 Conclusions
41

42 7.0 References

1 **APPENDIX E.3**
2 **OUTLINE OF TEST REPORT*·****
3
4
5 Table of Contents
6
7 Executive Summary
8
9 Introduction
10
11 I. Phase I PFOA Transport Testing
12
13   1. Experimental Apparatus
14   2. Description of Test Conditions (including deviations
15   from protocol)
16   3. Documentation of PFOA Standard
17   4. Analytical Results
18   4.1 PFOA
19   4.2 Total Fluorine
20   5. Transport Efficiency
21   5.1 PFOA
22   5.2 Total Fluorine
23   6. Discussion of Results
24   7. Conclusions
25
26 II. Phase II Incineration Testing (provided Phase II is performed)
27
28   1. Documentation of Test Substance Composites
29   2. Elemental Analysis Results
30   3. Combustion Stoichiometry Results
31   4. TGA Results
32   5. Combustion Testing
33   5.1 Experimental Apparatus
34   5.2 Description of Test Conditions (including deviations
35   from protocol)
36   5.3 Combustion Testing Results
37   5.3.1 Process Monitoring
38   5.3.2 Exhaust Gas Monitoring
39   5.3.2 Exhaust Gas Sampling and Analysis
40   5.3.2.1 PFOA
41   5.3.2.2 Fluoride
42   5.4 Discussion of Results
43   5.5 Conclusions
44
45 III. Appendices
46
47   • Quality Assurance Report(s)

1
2   • Report(s) from Compositing Facility(ies) (provided Phase II
3   is performed)
4
5   • Reports from Analytical Laboratories
6
7   • Release Assessment per Appendix E.2, if applicable
8
9
10
11   *   Test Report will include this information (as applicable)
12   but not necessarily in this order.
13
14   ** References to literature in this report will include full
15   citations.

APPENDIX F

UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY

TESTING CONSENT ORDER FOR THE LABORATORY-SCALE INCINERATION TESTING OF FLUOROTELOMER-BASED POLYMERS

EPA Docket No. OPPT - 2004 - 0001

Under the authority of section 4 of the Toxic Substances Control Act (TSCA), 15 U.S.C.

2603, the United States Environmental Protection Agency (EPA) issues this testing consent order

(Order) to take effect on the date of publication of the notice in the Federal Register announcing

the issuance of this Order. This Order incorporates the enforceable consent agreement (ECA) for

the laboratory-scale incineration testing of fluorotelomer-based polymer test substance

composites listed in Appendix A of the ECA.

Date

Susan B. Hazen
Principal Deputy Assistant Administrator
Office of Prevention, Pesticides and Toxic Substances

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APPENDIX F

UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY

TESTING CONSENT ORDER FOR THE LABORATORY-SCALE INCINERATION TESTING OF FLUOROPOLYMERS

EPA Docket No. OPPT - 2003 - 0071

Under the authority of section 4 of the Toxic Substances Control Act (TSCA), 15 U.S.C.

2603, the United States Environmental Protection Agency (EPA) issues this testing consent order

(Order) to take effect on the date of publication of the notice in the Federal Register announcing

the issuance of this Order. This Order incorporates the enforceable consent agreement (ECA) for

the laboratory-scale incineration testing of the fluoropolymer test substance composites listed in

Appendix A of the ECA.

_____
Date

_____
Susan B. Hazen
Principal Deputy Assistant Administrator
Office of Prevention, Pesticides and Toxic Substances

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