OPPT-2003-0071-0042

Robert J Giraud
<Robert.J.Giraud@US
A.dupont.com>

01/04/04 08:34 PM

To: Rich Leukroth/DC/USEPA/US@EPA, John
Blouin/DC/USEPA/US@EPA, Greg Fritz/DC/USEPA/US@EPA
cc: david.menotti@shawpittman.com, Stephen H Korzeniowski
<Stephen.H.Korzeniowski@USA.dupont.com>, Robert C Buck
<Robert.C.Buck@USA.dupont.com>, bill.beers@omnova.com
Subject: Re: Jan 6 ECA Development meeting - draft appendices and revised
draftappendices

Colleagues,

Attached are drafts of proposed ECA appendices B.1, D.1, D.2, and D.3. for
your review and comment:

(See attached file: App B.1 TGA Guideline 1-02-04.pdf)new appendix as
discussed

(See attached file: App D.1 Exhaust Gas Sampling draft 1-02-04.pdf)   new
appendix copied largely from Appendix C.5.2 of FP Incin Test Program draft
                          10-24-03 to facilitate it being
referred to from revised Appendix C.1 (transport testing)

(See attached file: App D.2 PFOA analysis draft 1-02-04.pdf)new appendix as
discussed

(See attached file: App D.3 Wickbold Torch draft 1-02-04.pdf)new appendix
as discussed

I am still working on completing Appendix D.4.

Please note that the reference to Appendix D.3 in Footnote 3 (p. 11) of ECA
cover document should be revised to reference to Appendix D.2 to match up
to revised numbering scheme for Appendix D.

Please also see attached revisions to Appendices C.1 and C.2 based on
recent drafting committee discussions.

(See attached file: App C.1 transport test 1-02-04.pdf)revised version of
10-24-03 Appendix B

(See attached file: App C.2 incin testing draft 1-02-04.pdf)revised version
of 10-24-03 Appendix C

As you can see, I have sharpened the focus on analytical parameters in
Appendix C.2 in light of recent GLP and QAPP discussions:

    dropped extraneous analyses for elemental analysis of test substance
    composites
    dropped bubbler analysis for total fluorine via Wickbold Torch (WT)
    during combustion testing because the LOQ for WT is several orders of
    magnitude higher than the LOQ for PFOA in water and orders of magnitude
    higher than the LOQ for fluoride ion in aqueous solution via ion
    chromatography
     dropped bubbler analysis for chloride ion as chloride is not a focus of
    this test program and is not believed present in many of the test
    substance composite components

Other revisions to Appendix C.2 are largely editorial in nature. For
example, the exhaust gas sampling section has been separated from exhaust
gas analysis section to simplify navigation thru the revised section
numbering scheme and because sampling and analysis are planned for
different locations.

1

I am sorry to say that my initial attempts at converting these documents to Word Perfect format have not been successful. I will check with my computer people on Monday in an effort to get as many of these to EPA as Word Perfect files as practicable in the next few days.

Please note that all of the above documents are draft and subject to revision once other member company representatives and UDRI have had an opportunity to review them.

I am still working on review of parts of each Appendix A.

I look forward to our discussions on Tuesday.

Thank you very much.

Best Regards,

Robert

App B.1 TGA Guideline 1-02-04.p App D.1 Exhaust Gas Sampling draft 1-02-04

App D.2 PFOA analysis draft 1-02-04. App D.3 Wickbold Torch draft 1-02-04.c App C.1 transport test 1-02-04.c

App C.2 incin testing draft 1-02-04.c

Appendix B.1
Guideline for Thermogravimetric Analysis

ASTM E 1868-02 "Standard Test Method for Loss-On-Drying by Thermogravimetry" will be used as the guideline for conducting the analysis described in Appendix C.2.3 with the following exceptions:

Section	Exception
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.
4.1	• The loss-on-drying (LOD) value specified in the second through fifth sentences of this section will not be recorded.
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 0.05 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" noted in this section will be 5 min.
11.10.1.1	• LOD values will not be recorded.
12.1	• The LOD 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 LOD 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.

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

1 **APPENDIX 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 250 °C (based on
28 thermogravimetric analysis of PFOA) with transfer line and
29 reactor temperatures 0 to 100 °C higher than the
30 gasification temperature.
31
32 Three replicate transport efficiency test runs will be
33 conducted. A minimum of one blank run will be conducted
34 prior to each transport efficiency test run.
35
36 The sample size of the PFOA standard to be gasified will be
37 less than 5 mg. The reactor exhaust gas will be collected
38 into bubbler aqueous solution as described in Appendix D.1
39 (including an HPLC water rinse of the flexible tubing used
40 to connect the thermal reactor system and the bubbler
41 assembly into the aqueous solution composite), which will
42 be analyzed for PFOA as described in Appendix D.2. In
43 order to provide a second way of demonstrating quantitative
44 transport, this aqueous solution composite will also be
45 analyzed for total fluorine as described in Appendix D.3.
46 (Testing for total fluorine is included due to possibility
47 of thermal degradation of PFOA under transport test

1 conditions.) Therefore, for this transport testing the
2 sample size of PFOA standard will be sufficiently high to
3 assure that the total fluorine input to the thermal reactor
4 system will be greater than 140% of the mass corresponding
5 to the limit of quantitation (LOQ) for total fluorine in
6 the aqueous solution composite. (The LOQ for total
7 fluorine in aqueous solution is much higher than the LOQ
8 for PFOA in aqueous solution.)
9
10 The amount of PFOA and total fluorine in the thermal
11 reactor system exhaust gas will be determined via analysis
12 of the aqueous solution composite as noted above.
13
14 The amount of PFOA fed to the thermal reactor system will
15 be known based on measurement prior to gasification and
16 will be verified by weighing the pyroprobe insert cartridge
17 before and after each test run. The amount of fluorine fed
18 to the system will be calculated from the amount of PFOA
19 fed, the known purity of the PFOA, and the known fluorine
20 fraction of the PFOA standard.
21
22 PFOA transport efficiency (TE) as a percentage will be
23 computed as follows:
24
25 % PFOA TE = mass of PFOA in aqueous solution composite * 100   (1)
26   mass of PFOA fed to thermal reactor system
27
28 Total fluorine (TF) transport efficiency as a percentage
29 will be computed as follows:
30
31 % Total F TE = mass of total F in aqueous solution composite * 100 (2)
32   mass of total F fed to thermal reactor system
33
34 If the transport efficiencies for both PFOA (equation 1)
35 and total fluorine (equation 2) are less than or equal to
36 70%, then additional work will be performed as described in
37 Section C.1.2.2.
38
39 C.1.2.2 Contingent Testing
40
41 As indicated by Section C.1.2.1, additional work will be
42 performed, as necessary, in a step-wise fashion to
43 determine if consideration of one or more of the following
44 procedural revisions enables achievement of 70% transport
45 efficiency as follows:
46
47 1. The flexible tubing between the thermal reactor system
48   and the bubbler assembly from the experiment described in

C.1-2

1   Section C.1.2.1 would be quantitatively rinsed with
2   methanol. This methanol rinsate would be analyzed for
3   PFOA (as described in Appendix D.2) and/or for total
4   fluorine (as described in Appendix D.3). Revised
5   transport efficiency (TE) as a percentage for PFOA
6   (equation 3) and/or total fluorine (equation 4) would be
7   computed by including the mass of analyte in the methanol
8   rinse in the numerator as follows:

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

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

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

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

2. Reagent(s) would be added to the bubbler aqueous
   solution, and the experiment described in Section C.1.2.1
   would be repeated 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 B.2 would be determined.

C.1.3 Reporting of Results

Following completion of PFOA transport testing as described
in this appendix and prior to beginning incineration
testing described in Appendix C.2, a brief letter report
will be submitted to EPA with the transport efficiency
result(s).

If Appendix C.2 incineration testing is performed, the

1 detailed results of Appendix C.1 transport testing will be
2 included in the final report for Appendix C.2 incineration
3 testing.   If Appendix C.2 incineration testing is not
4 performed, the detailed results of Appendix C.1 transport
5 testing will be provided in a test report for Appendix C.1
6 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 to aid in preparation for combustion testing
10 described in Section C.2.4.
11
12 As Kissa (1998) points out, technique strongly affects
13 analytical results for fluorinated organic compounds such
14 as fluorinated surfactants and fluorinated polymers due to
15 the strength of the carbon-fluorine bond:
16
17   Fluorine in organic compounds is usually determined by
18   converting organic fluorine to an inorganic fluoride.
19   Various combustion methods are routinely used for this
20   purpose. However, the carbon-fluorine bond is
21   exceptionally strong, and extremely vigorous conditions are
22   needed for a quantitative mineralization. Conventional
23   combustion conditions used for the determination of carbon
24   and hydrogen in nonfluorinated organic compounds are not
25   adequate for a quantitative analysis of fluorinated
26   surfactants.
27
28 Therefore, total fluorine analysis will be performed using
29 "extremely vigorous conditions" as described in Section
30 C.2.1.2, and the commercially available conventional
31 technique used for empirical determination of carbon and
32 hydrogen content (described in Section C.2.1.3) will
33 provide estimated values.
34
35 C.2.1.2 Total Fluorine
36
37 Each test substance composite will be characterized via
38 analysis of total fluorine content.
39
40 Based on manufacturing process knowledge, the levels of
41 total fluorine in the components of test substance
42 composites are orders of magnitude higher than the
43 potential trace level of inorganic fluoride in these
44 materials. Therefore, for this test program, the total
45 organic fluorine value for each test substance composite
46 will be considered to be the same as the total fluorine
47 value.
48
49 Total fluorine content will be measured via the Wickbold

C.2-1

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

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

25
26 C.2.1.3.2 Empirical Determination
27
28 Where compositional information on carbon and hydrogen
29 content is not known from the identity of the components in
30 a given composite, each such test substance composite will
31 be analyzed for carbon and hydrogen.
32
33 As noted in Section C.2.1.1, empirical determination of
34 carbon in test substance composites via commercially
35 available conventional techniques is expected to
36 underestimate the carbon content of the sample due to the
37 strength of the carbon-fluorine bond. Similarly, empirical
38 determination of hydrogen in test substance composites via
39 commercially available conventional techniques is expected
40 to overestimate the hydrogen content of the sample.
41
42 The carbon content of the sample is measured by determining
43 the carbon dioxide (CO_2) generated by the oxidation of the

1 sample. This oxidation may be accomplished by high
2 temperature combustion, catalytic combustion, or wet
3 chemical oxidation. The CO_2 is measured directly by an
4 infrared detector or a thermal conductivity detector, via
5 absorption into a suitable solution (e.g., potassium
6 hydroxide) and gravimetric determination, or by conversion
7 to methane for measurement via a flame ionization detector.
8
9 The hydrogen content of the sample can be determined by
10 difference with knowledge of the fluorine content and
11 carbon content of the sample where the moisture content and
12 chlorine content of the sample are negligible or known.
13 Alternatively, the hydrogen content of the sample is
14 measured by determining the water generated by high
15 temperature combustion of the sample. Measurement of water
16 in the combustion gas for this analysis may be accomplished
17 by techniques such as use of an infrared detector or
18 absorption on a dessicant with gravimetric determination.
19 With empirical hydrogen determination, it is important to
20 correct for the water in the combustion gas attributable to
21 the moisture content in the sample to obtain the hydrogen
22 content of the sample; see Section C.2.1.4.
23
24 Manufacturing process knowledge of the polymers will be
25 used to review the elemental analysis results and to form
26 the basis for interpreting non-detects. For example, if
27 the hydrogen analytical result for a perfluorinated polymer
28 is less than a quantitation limit of 0.1%, then the
29 analytical result will be replaced with 0.
30
31 C.2.1.4 Moisture
32
33 Where preparation (as described in Appendix A.4) for a
34 given test substance composite has involved dewatering, the
35 moisture (or solids) content of each such test substance
36 composite will be determined in order to provide a dry
37 basis for calculations as needed.
38
39 Moisture is determined by measuring the loss of weight of
40 the sample when heated under controlled conditions. A
41 representative sample is weighed and placed in a crucible
42 (or dish) and evaporated to dryness in an air or nitrogen
43 atmosphere at a defined temperature setpoint (e.g., 103 °C
44 to 105 °C) in the range of 100 °C to 125 °C.
45
46 The moisture value is calculated as the loss in weight
47 (difference between the starting weight of sample and the

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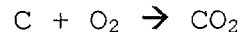13 converted to molar quantities on a dry basis.
14
15 Second, based on Chapter 3 of *Combustion Fundamentals for*
16 *Waste Incineration* (American Society of Mechanical
17 Engineers, 1974), the reaction products for these molar
18 quantities are calculated assuming complete combustion with
19 the following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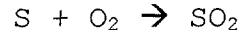21   a) All carbon (C) in feed converts to carbon dioxide (CO_2)
22         $C + O_2 \rightarrow CO_2$
23
24   b) All sulfur (S) in feed converts to sulfur dioxide (SO_2)
25         $S + O_2 \rightarrow SO_2$
26
27   c) The halogens (Cl, F) in feed convert to hydrogen halides
28         $H_2 + Cl_2 \rightarrow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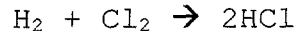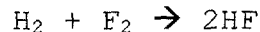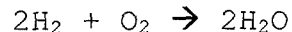
1 Note that the term feed in the preceding rules (a through
2 e) includes both material being combusted and the fuel
3 source of hydrogen such as methane or methanol.
4 Additionally, stoichiometric calculations as described
5 above presume that the compounds undergoing combustion are
6 essentially free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

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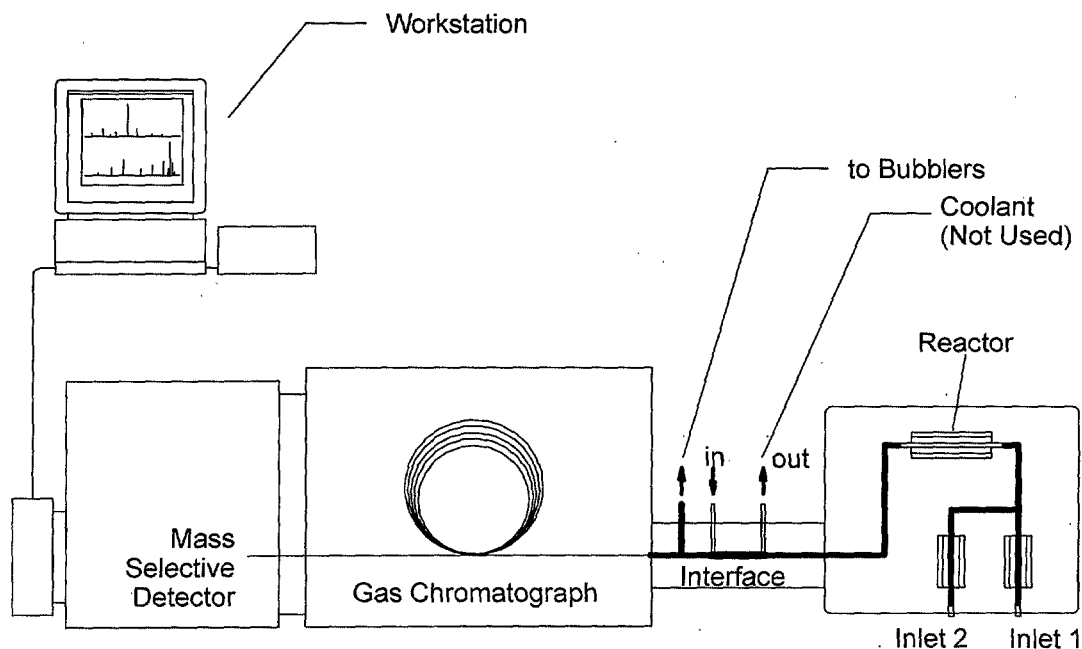
26
27 The ATRS consists of a reactor assembly and in-line gas
28 chromatograph/detector system connected via an interface.

1   The reactor assembly consists of a thermally insulated
2   enclosure housing the sample introduction, reactor, and
3   transfer line systems.
4
5   Sample introduction for solid materials (Inlet 1) employs a
6   pyroprobe, a device designed to gasify samples by heating
7   them at a fixed rate. The main gas flow will also be fed
8   via Inlet 1, and Inlet 2 will be used to feed supplemental
9   flow.
10
11 During combustion tests, the transfer line between the
12 pyroprobe and the reactor is heated and maintained above
13 200 °C. The reactor is housed within its own small tube
14 furnace and may be independently heated to as high as 1100
15 °C. (Actual conditions for this test program are presented
16 in Section C.2.4.3.) The transfer line from the reactor to
17 the interface is heat traced to greater than 200 °C to
18 prevent cool regions where reactor products could otherwise
19 be lost through condensation.
20
21 The interface routes the combustion exhaust gas to the in-
22 line gas chromatograph (GC) and mass selective detector
23 (MSD) or to sample collection for off-line analysis. For
24 combustion testing in this test program, the interface will
25 also be maintained above 200 °C. Exhaust gas monitoring for
26 this program is described in Section C.2.4.5.
27
28 C.2.4.3 Combustion Test Experimental Conditions
29
30 Each test substance composite will be subjected to
31 laboratory-scale incineration using the experimental
32 apparatus described in Section C.2.4.2.
33
34 C.2.4.3.1 Combustion Air
35
36 Synthetic air (mixture of 21% oxygen and 79% nitrogen) will
37 be used in place of compressed air to prevent potential
38 interference in the experimental system due to background
39 levels of CO_2 in compressed air.
40
41 C.2.4.3.2 Fuel
42
43 Methanol will be used, as needed, as a supplemental fuel to
44 ensure the presence of sufficient hydrogen to convert
45 fluorine to hydrogen fluoride (HF) and chlorine to hydrogen
46 chloride (HCl).
47

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

20
21 These conditions are representative of typical furnace
22 operating conditions of municipal waste combustors (MWCs)
23 and of typical secondary chamber operating temperatures for
24 medical waste incinerators in the U.S. See Appendix D.4
25 for supporting information.
26
27 Temperature and residence time values in Table C.2-2 will
28 be fixed setpoints for the experiment. The temperature of
29 the high temperature reactor will be controlled within ±10
30 °C to assure isothermal operation.
31
32 The ATRS sample size for the test substance composites in
33 this testing program will be a measured amount less than 5
34 mg. The actual sample size, gasification rate (determined
35 from TGA), air supply, and fuel supply will be adjusted to
36 assure that the oxygen level in the exhaust will be greater
37 than or equal to the concentration in Table C.2-1
38 throughout each test to be representative of typical MWC
39 conditions. The fuel supply and air supply will also be
40 adjusted as needed to approach the target H_2O concentration
41 in exhaust gas in Table C.2-1.
42

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

29
30 Temperature-Inlet 1 will be recorded at the end of the
31 temperature ramp-up for gasification to monitor the
32 pyroprobe final temperature.
33
34 The flow rate of the exhaust gas routed to the bubblers (see
35 Section C.2.4.5.2) will be determined based on the flow
36 measurements listed in Table C.2-2.

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

1 method detection limit (MDL) will be reported as ND, sample
2 results between MDL and the limit of quantitation (LOQ)
3 will be reported as NQ, and numerical values will not be
4 reported for such samples.
5
6 Due to background levels of PFOA, the analytical laboratory
7 will only report numerical values for PFOA concentration in
8 the aqueous solution greater than or equal to the LOQ.
9 This is required to assure that the reported concentration
10 value is attributable to the sample rather than to
11 background.
12
13 C.2.4.8 Test Substance Sampling & Analysis
14
15 See Section C.2.1. (Elemental Analysis)
16
17 C.2.5 Reporting of Results
18
19 C.2.5.1 Elemental Analysis Results
20
21 The results of elemental analysis of the test substance
22 composites (as noted in Section C.2.1) will be reported.
23 The laboratory reports will be included in an appendix to
24 the test report.
25
26 C.2.5.2 Combustion Stoichiometry Results
27
28 Combustion stoichiometry (as noted in Section C.2.2)
29 calculations will be included in an appendix to the test
30 report.
31
32 C.2.5.3 TGA Results
33
34 TGA graphical results for test substance composites (as
35 noted in Section C.2.3) will be included in an appendix to
36 the test report.
37
38 C.2.5.4   Combustion Test Results
39
40 C.2.5.4.1 Process Monitoring
41
42 Process monitoring data (as noted in Section C.2.4.4)
43 recorded for each combustion test will be reported in
44 tabular form.
45
46 C.2.5.4.2 Exhaust Gas Monitoring
47

1 Exhaust gas O_2, CO and CO_2 monitoring results will be
2 reported as the integrated or average value for each
3 combustion test. CO will be reported in terms of parts per
4 million by volume (ppmv). O_2 and CO_2 will be reported in
5 terms of percent by volume (%).
6
7 C.2.5.4.3 Exhaust Gas Analytical Results
8
9 Results of analyses noted in Section C.2.4.5.2 will be
10 reported for each combustion test.
11
12 The analytical result for each analyte in Section C.2.4.5.2
13 will be reported in terms of concentration (mass per
14 volume) in the bubbler aqueous solution. For each analyte,
15 this value will be used with the associated exhaust gas
16 volume to compute an exhaust gas concentration and with the
17 associated test substance mass to compute mass of analyte
18 per mass of test substance composite.
19
20 C.2.5.4.3.1 Fluoride
21
22 Fluoride ion in the exhaust gas will be reported on the
23 basis of mass of fluoride ion per mass of test substance
24 composite. The corresponding hydrogen fluoride value for
25 each will also be computed and reported for reference.
26
27 C.2.5.4.3.2 PFOA
28
29 PFOA results for the bubbler aqueous solution samples will
30 be reported as described in Section C.2.4.7.2. PFOA
31 results for associated blanks will also be reported.
32
33 If present in the bubbler aqueous solution at a
34 concentration above the matrix-specific LOQ, PFOA in the
35 exhaust gas will be reported on the basis of mass of PFOA
36 per mass of test substance composite.
37
38 C.2.5.5 Test Substance Results
39
40 Elemental compositions will be reported as indicated in
41 Section C.2.4.6.1 above.
42
43 C.2.5.6 Release Assessment
44
45 In the event that PFOA is found in the exhaust gas bubbler
46 aqueous solution at a concentration above the LOQ for the
47 three runs for a given test substance composite, then the

1   potential for release from full-scale municipal and/or
2   medical waste incineration (including application of air
3   pollution controls) of the subject material in the U.S.
4   will be assessed to inform the basis for possible next
5   steps.
6
7   This assessment will consider a number of factors such as
8
9   • PFOA results from this testing program reported per
10   Section C.2.5.4.3.2,
11   • estimated concentration of subject material in feed to
12   applicable type(s) of full-scale waste incinerators
13   (based on such information as Appendix A.2, supplemental
14   information on material applications, and available
15   information on hydrogen fluoride concentration in waste
16   incinerator exhaust as upper bound), and
17   • use and abatement effectiveness of common post-combustion
18   air pollution control equipment (e.g., lime scrubbing,
19   carbon adsorption) employed by typical operating full-
20   scale waste incinerators.
21
22   See Appendix E.2 for the draft outline of the Release
23   Assessment report in case this report is to be submitted.

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 empty bubbler will be added to the front end
20 of this series of bubblers to serve as a knock-out pot if
21 calculations or preliminary measurements indicate that
22 greater than 10 mL of water will be produced during the
23 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 C_{18} solid phase
27 extraction (SPE) cartridge. PFOA is eluted from the
28 cartridge with methanol. Quantification of PFOA is
29 accomplished by liquid chromatography/tandem mass
30 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 distinct from blanks and spikes, such as
44 the types of samples generated by the testing programs
45 described in Appendix C, as follows:
46
47   Field samples in which either no peaks or peaks less than the

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

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).
3.5 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.

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 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
23
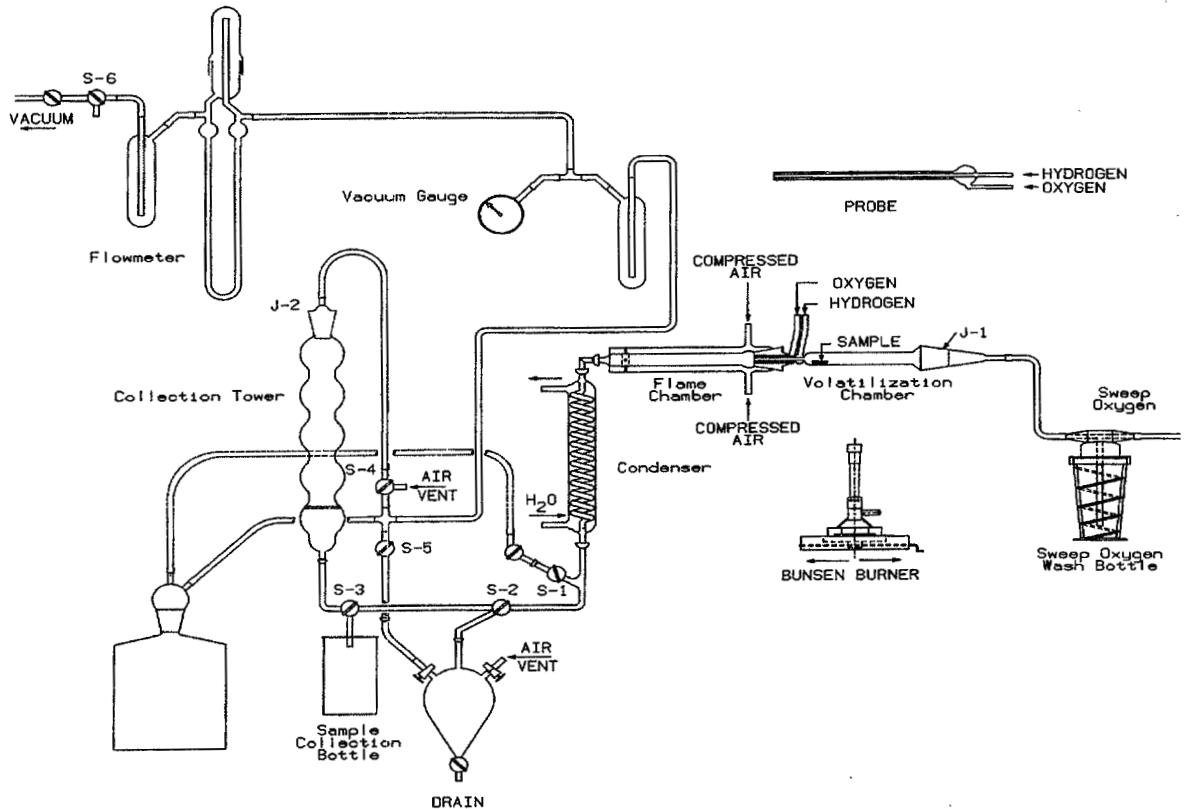
1   ## D.3.3 Method Description

2

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

5

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

14

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

17

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

24

25 ## D.3.4 Safety Considerations

26

27 Use of hydrogen presents a potential fire and explosion
28 hazard. Use of oxygen presents a potential fire hazard.
29 Safe operation of the oxyhydrogen torch requires the use of
30 specialized equipment with shielding and elaborate safety
31 devices by well-trained personnel.

32

33 ## D.3.5 References

34

35 Kissa, E. "Analysis of Anionic Fluorinated Surfactants",
36 Chapter 8 in Anionic Surfactants: Analytical Chemistry –
37 2nd Edition, Revised and Expanded, edited by John Cross.
38 Marcel Dekker Surfactant Science Series, volume 73, 1998.

39

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