

54P55

OPPT-2003-0091-0056



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01/20/04 06:54 AM

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Subject: materials and call-in number for fluoropolymers incin testing ECA conf
callon Wed Jan 21

Colleagues,

As Rich has noted, our next fluoropolymers incineration testing ECA drafting committee call is scheduled for Wednesday January 21 from 7 am to 9 am ET. The call-in details for people in the U.S. are as follows:

phone number: [REDACTED]
code: [REDACTED]

I understand that the goal of our call is to enable assembly of a complete draft ECA (including all the appendices) for distribution as a draft to interested parties in advance of the upcoming Technical Working Group meeting and to have language acceptable to drafting committee members and with open issues identified.

To that end, please see the attached documents; these documents are being sent to both incineration testing ECA drafting committees as many of them are likely to be relevant to both. Please note that they are all draft subject to revision once FMG and TRP member companies complete their reviews of these documents.

Additionally, given the the charge to prepare a complete draft ECA, I have put considerable time into preparing the attached documents below, which took time away from completing the GLP review that I began in December. Therefore, as you can see a GLP tailoring discussion document is not provided. Nevertheless, David and I are prepared for some GLP discussion during the drafting committee conference call.

Draft Appendix D.4 is attached:

(See attached file: App D.4 WasteIncin Op Conditions DRAFT 1-20-04.pdf)

Draft of complete Table 1 for Telomers (the test program to go first) without the need for "?????" is attached:

(See attached file: Incin Testing Table 1 - Telomers draft 1-20-04.pdf)

Please note that this is all one table with one common set of sequential footnotes even though it is 2 pages long.

Also, please note that the Table 1 for Fluoropolymers is a bit more complicated due to the need for sequencing thru some of the same equipment as we have discussed and the need for multiple compositing labs. Therefore, the Table 1 for Fluoropolymers without the need for "?????" has not yet been prepared

Attached is draft Appendix G addressing content of QAPPs as referenced in Table 1:

(See attached file: App G QAPP Outline draft 1-20-04.pdf)

Please note that from this point forward in the message all attachments are revisions of appendices previously discussed by the drafting committee.

Revised draft Appendix C.2 marked up per the Jan. 6, 2004 drafting

1

committee conference call is attached:

(See attached file: App C.2 incin testing draft 1-20-04.pdf)

Based on completion of Appendix D.4 (indicating that the amount of medical waste burned annually is no more than 1% of the amount of municipal waste burned annually in the U.S.), I have not revised the last sentence of Section C.2.4.1 since conditions representative of typical MWC operations are the focus of this work.

Please note that the target exhaust water concentration has been revised to 15% (up from 14%) based on completion of Appendix D.4 above. Any other changes to C.2 (which are clearly marked are based on discussion with Phil Taylor. Phil and I agree that the term "experiment" should stay where it is used in this appendix.

Attached is another copy of draft Appendix C.2 without tracking changes just in case it is ready as is:

(See attached file: App C.2 incin testing draft 1-20-04-not-marked.pdf)

Revised draft Appendix E.2 based on Jan. 6 drafting committee conference call as well as on the Dec. 22 drafting committee conference call is attached:

(See attached file: App E.2 release assess outline draft 1-20-04.pdf)

I am sorry that changes in revised E.2 are not tracked in the document.

Revised draft appendices without strike and insert format as agreed to during the January 13 drafting committee call are as follows:

(See attached file: App B.1 TGA Guideline draft 1-19-04.pdf)

(See attached file: App D.1 Exhaust Gas Sampling draft 1-19-04.pdf)

(See attached file: App D.2 PFOA analysis draft 1-19-04.pdf)

(See attached file: App D.3 Wickbold Torch draft 1-19-04.pdf)

I would be glad to compile the appendices into a single electronic PDF file if that would help. Receiving EPA Appendix A text saved as a WORD document or in RTF format would make this go faster.

I look forward to our upcoming discussions.

Best Regards,

Robert Giraud

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App D.4 Waste Incin Op Conditions DRAFT 1-20-04 Incin Testing Table 1 - Telomers draft 1-20-04

App G QAPP Outline draft 1-20-04. App C.2 incin testing draft 1-20-04.

App C.2 incin testing draft 1-20-04-not-marked App E.2 release assess outline draft 1-20-04

App B.1 TGA Guideline draft 1-19-04. App D.1 Exhaust Gas Sampling draft 1-19-04

App D.2 PFOA analysis draft 1-19-04. App D.3 Wickbold Torch draft 1-19-04.

1 **Table 1. REQUIRED TESTING, TEST STANDARDS, AND REPORTING**
 2 **FOR LABORATORY-SCALE INCINERATION TESTING OF FLUOROTELOMER-**
 3 **BASED POLYMERS**
 4

Phase I PFOA Transport Testing	Requirement or Test Standard	Deadline for Submission (Months)
Study Plan(s)	40 CFR 790.62(b) as annotated by Part X. of ECA	2 ¹
QAPP	Appendix G.	3 ¹
Quantitative PFOA transport testing	Appendix C.1	8 ^{2,3,4,5}

5
 6 1 Number of months after the effective date of the ECA when this
 7 submission is due to EPA.

8
 9 2 Number of months after EPA approval of Study Plan(s) and QAPP for
 10 Phase I testing when a letter report with transport efficiency
 11 result(s) and indication of what contingent testing, if any, was
 12 performed is due to EPA, provided that the Study Plan(s) and QAPP are
 13 approved by EPA within 2 months of submission. If this Study Plan(s)
 14 and this QAPP are not approved within 2 months of submission, then this
 15 deadline is extended by 6 months.

16
 17 3 In the event that the transport efficiency of PFOA or of total
 18 fluorine (as determined by the formulas in Appendix C.1) is greater
 19 than or equal to 70%, then the Companies will proceed to Phase II
 20 Incineration Testing. In the event that the transport efficiency of
 21 both PFOA and total fluorine (as determined by the formulas in Appendix
 22 C.1) is less than 70%, then the Companies will initiate a Technical
 23 Consultation with EPA to reach agreement on a path forward. The
 24 outcomes of the Technical Consultation are described in Part VIII of
 25 this ECA.

26
 27 4 The final report for Phase I testing will be submitted to EPA
 28 within 60 days of the completion of the Technical Consultation if this
 29 consultation does not result in an agreement to conduct further
 30 testing. If the technical consultation results in an agreement to
 31 conduct further testing, the final report for Phase I testing will be
 32 included in the final test report for such testing, unless agreed
 33 otherwise in the Technical Consultation.

34
 35 5 Interim progress reports, following the outline in Appendix E.1,
 36 must be submitted by the Companies to EPA every 6 months beginning six
 37 months from the effective date of the this ECA until the end of this
 38 ECA testing program.
 39

1

Phase II Incineration Testing for Test Substance Composites	Requirement or Test Standard	Deadline for Submission (Months)
Study Plan(s)	40 CFR 790.62(b) as annotated by Part X. of ECA	2 ¹
QAPP	Appendix G.	6 ¹
Each component from each company sent to each applicable facility designated by the Companies	Company-specific signature page and Appendix A	2 ⁷
Elemental Analysis ⁶	Appendix C.2.1	24 ^{7,8}
Combustion Stoichiometry ⁶	Appendix C.2.2	24 ^{7,8}
Thermogravimetric Analysis ⁶	ASTM E1868 as modified in Appendix B.1	24 ^{7,8}
Laboratory-scale Combustion Testing ⁶	Appendices C.2.4 and C.2.5 as supplemented by Appendices D.1, D.2, and D.3, and Appendix E.2 (if indicated)	24 ^{7,8}

2

3

6 The results of this testing will be provided in the final report for Phase II.

4

5

6

7 Number of months from submission of the Phase I testing letter report, if Phase II testing is required by the results of Phase I testing (see footnote 3), that the final report for this testing is due to EPA. If the Study Plan(s) and QAPP for Phase II testing are not approved within 2 months of submission of the QAPP to EPA, then this deadline is extended by 6 months. If Phase II testing is required by Technical Consultation agreement (see footnote 3), the deadline for submission shall be as agreed in the technical consultation. Where the same type of testing (e.g., PFOA analysis) is performed in Phase II as in Phase I, Phase II QAPP provisions relevant to such testing will be deemed to be approved by EPA upon EPA approval of the relevant provisions of the Phase I QAPP.

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8 Interim progress reports, following the outline in Appendix E.1, must be submitted by the Companies to EPA every 6 months beginning six months from the effective date of this ECA until the end of this ECA testing program.

§

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 modifications for this testing program:

Section	Modification
2.1	<ul style="list-style-type: none"> 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	<ul style="list-style-type: none"> The loss-on-drying value specified in the second through fifth sentences of this section will not be recorded.
7.1.3	<ul style="list-style-type: none"> 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 $\pm 3^\circ\text{C}$, rather than $\pm 2^\circ\text{C}$.
7.1.4	<ul style="list-style-type: none"> 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	<ul style="list-style-type: none"> 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 $\pm 3^\circ\text{C}/\text{min}$, rather than $\pm 0.1^\circ\text{C}/\text{min}$. Within the range of 25 to 1000°C, the isothermal temperature will be maintained within $\pm 3^\circ\text{C}$, rather than $\pm 2^\circ\text{C}$.
11.4	<ul style="list-style-type: none"> 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	<ul style="list-style-type: none"> 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	<ul style="list-style-type: none"> 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.

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.

APPENDIX C.2**INCINERATION TESTING****C.2.1 Elemental Analysis**

C.2.1.1 Introduction

Elemental analysis as described in Section C.2.1 will be performed for each test substance composite to aid in preparation for combustion testing described in Section C.2.4.

As Kissa (1998) points out, technique strongly affects analytical results for fluorinated organic compounds such as fluorinated surfactants and fluorinated polymers due to the strength of the carbon-fluorine bond:

Fluorine in organic compounds is usually determined by converting organic fluorine to an inorganic fluoride. Various combustion methods are routinely used for this purpose. However, the carbon-fluorine bond is exceptionally strong, and extremely vigorous conditions are needed for a quantitative mineralization. Conventional combustion conditions used for the determination of carbon and hydrogen in nonfluorinated organic compounds are not adequate for a quantitative analysis of fluorinated surfactants.

Therefore, total fluorine analysis will be performed using "extremely vigorous conditions" as described in Section C.2.1.2, and the commercially available conventional technique used for empirical determination of carbon and hydrogen content (described in Section C.2.1.3) will provide estimated values.

C.2.1.2 Total Fluorine

Each test substance composite will be characterized via analysis of total fluorine content.

Based on manufacturing process knowledge, the levels of total fluorine in the components of test substance composites are orders of magnitude higher than the potential trace level of inorganic fluoride in these materials. Therefore, for this test program, the total organic fluorine value for each test substance composite will be considered to be the same as the total fluorine value.

C.2-1

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1 Total fluorine content will be measured via the Wickbold
2 Torch method; see Appendix D.3.

3
4 C.2.1.3 Carbon and Hydrogen

5
6 In order to provide information for stoichiometric
7 calculations in Section C.2.2, the carbon and hydrogen
8 content of each test substance composite is needed. Based
9 on manufacturing process knowledge of the polymers in this
10 program, levels of sulfur, and nitrogen are expected to be
11 less than 0.1% and to thereby have negligible effect on
12 stoichiometric calculations.

13
14 C.2.1.3.1 Theoretical Determination

15
16 Where the elemental composition of a test substance
17 composite is known from the identity of the components in a
18 given composite, the carbon and hydrogen content of the
19 test substance composite can be calculated.

20
21 For example, where each of the components of a test
22 substance composite are polytetrafluoroethylene (PTFE), the
23 carbon and hydrogen can be determined knowing the molecular
24 formula for PTFE is $(C_2F_4)_n$ as follows:

25

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

26
27 C.2.1.3.2 Empirical Determination

28
29 Where compositional information on carbon and hydrogen
30 content is not known from the identity of the components in
31 a given composite, each such test substance composite will
32 be analyzed for carbon and hydrogen.

33
34 As noted in Section C.2.1.1, empirical determination of
35 carbon in test substance composites via commercially
36 available conventional techniques is expected to
37 underestimate the carbon content of the test substance
38 composites due to the strength of the carbon-fluorine bond.
39 Similarly, empirical determination of hydrogen in test
40 substance composites via commercially available
41 conventional techniques is expected to overestimate the
42 hydrogen content of the test substance composites.

43

C.2-2

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1 The carbon content of the test substance composite can be
2 measured by determining the carbon dioxide (CO₂) generated
3 by the oxidation of the sample. This oxidation may be
4 accomplished by high temperature combustion, catalytic
5 combustion, or wet chemical oxidation. The CO₂ is measured
6 directly by an infrared detector or a thermal conductivity
7 detector, via absorption into a suitable solution (e.g.,
8 potassium hydroxide) and gravimetric determination, or by
9 conversion to methane for measurement via a flame
10 ionization detector.

11

12 The hydrogen content of the sample can be determined by
13 difference with knowledge of the fluorine content and
14 carbon content of the sample where the moisture content and
15 chlorine content of the sample are negligible or known.
16 Alternatively, the hydrogen content of the sample is
17 measured by determining the water generated by high
18 temperature combustion of the sample. Measurement of water
19 in the combustion gas for this analysis may be accomplished
20 by techniques such as use of an infrared detector or
21 absorption on a desiccant with gravimetric determination.
22 With empirical hydrogen determination, it is important to
23 correct for the water in the combustion gas attributable to
24 the moisture content in the sample to obtain the hydrogen
25 content of the sample; see Section C.2.1.4.

26

27 Manufacturing process knowledge of the polymers will be
28 used to review the elemental analysis results and to form
29 the basis for interpreting non-detects. For example, if
30 the hydrogen analytical result for a perfluorinated polymer
31 is less than a quantitation limit of 0.1%, then the
32 analytical result will be replaced with 0.

33

34 C.2.1.4 Moisture

35

36 Where preparation (as described in Appendix A.4) for a
37 given test substance composite has involved dewatering, the
38 moisture (or solids) content of each such test substance
39 composite will be determined in order to provide a dry
40 basis for calculations as needed.

41

42 Moisture is determined by measuring the loss of weight of
43 the sample when heated under controlled conditions. A
44 representative sample is weighed and placed in a crucible
45 (or dish) and evaporated to dryness in an air or nitrogen
46 atmosphere at a defined temperature setpoint (e.g., 103 °C
47 to 105 °C) in the range of 100 °C to 125 °C.

C.2-3

1 The moisture value is calculated as the loss in weight
2 (difference between the starting weight of sample and the
3 final weight of sample) divided by the starting weight of
4 sample. Similarly, a solids value can be calculated as the
5 final weight of sample divided by the starting weight of
6 sample.

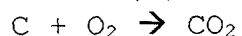
8 **C.2.2 Combustion Stoichiometry**

9
10 Combustion stoichiometry calculations as described in
11 Section C.2.2 will be performed to aid in preparation for
12 combustion testing described in Section C.2.4

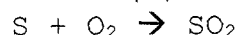
13
14 First, the weight percent values from Section C.2.1 are
15 converted to molar quantities on a dry basis.

16
17 Second, based on Chapter 3 of *Combustion Fundamentals for*
18 *Waste Incineration* (American Society of Mechanical
19 Engineers, 1974), the reaction products for these molar
20 quantities are calculated assuming complete combustion with
21 the following rules:

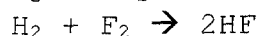
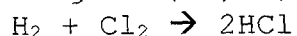
22
23 a) All carbon (C) in feed converts to carbon dioxide (CO₂)



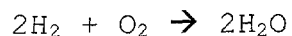
25
26 b) All sulfur (S) in feed converts to sulfur dioxide (SO₂)



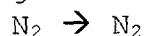
28
29 c) The halogens (Cl, F) in feed convert to hydrogen halides



32
33 d) Hydrogen (H) present in feed in excess of that
34 required to yield products in item c) above will be
35 converted to water

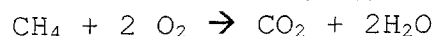


37
38 e) Nitrogen (N) from feed or air is emitted as molecular
39 nitrogen



41
42 Third, with these rules, the balanced chemical reaction for
43 combustion of a compound can be written.

44
45 For example, the resulting reaction equation for a
46 hydrocarbon like methane (CH₄) is



C.2-4

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

C.2-5

1 conditions representative of typical municipal waste
2 combustor operations in the U.S.

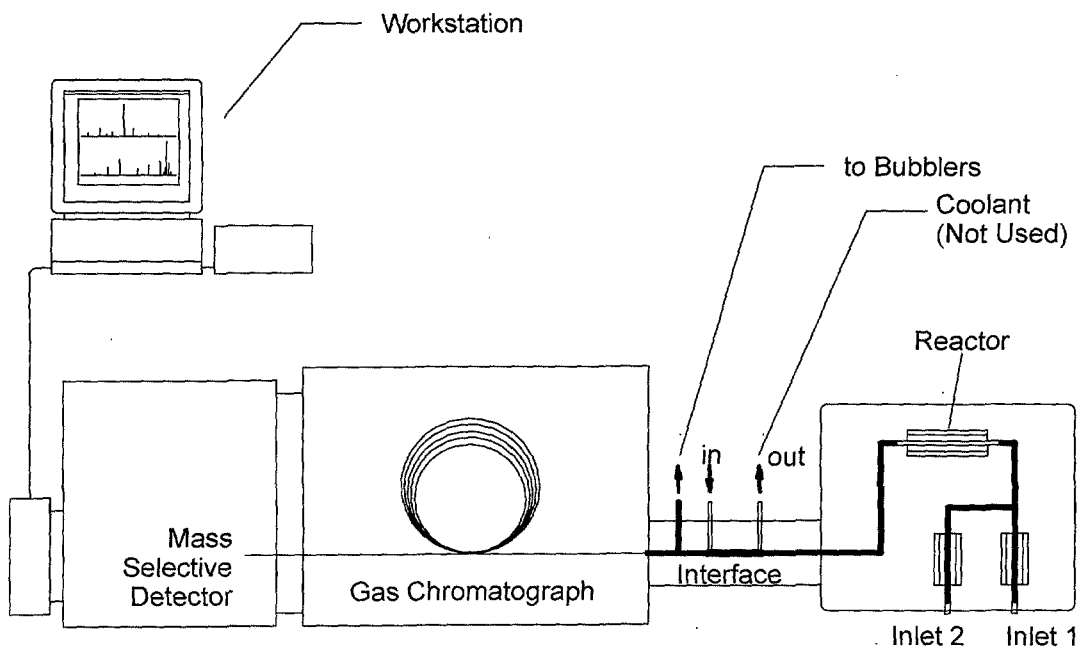
3 4 C.2.4.2 Experimental Apparatus

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.

C.2-6

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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 CO₂ 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

C.2-7

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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 ₂ O concentration in exhaust gas	15%
Number of replicate runs	3

20
21 These conditions are conservatively representative of
22 typical furnace operating conditions of municipal waste
23 combustors (MWCs) and of typical secondary chamber
24 operating temperatures for medical waste incinerators in
25 the U.S. See Appendix D.4 for supporting information.

26
27 Temperature and residence time values in Table C.2-2 will
28 be fixed setpoints for these experiments. The temperature
29 of the high temperature reactor will be controlled within
30 +10 °C to assure isothermal operation.

31
32 The amount of each test substance composite fed to the ATRS
33 in this testing program will be a measured amount less than
34 5 mg. The actual amount fed, 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 H₂O concentration
41 in exhaust gas in Table C.2-1.

42

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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 results; see Section
6 C.2.3. This is necessary to assure complete gasification
7 of the sample of test substance composite and a common set
8 of experimental conditions across the test materials during
9 combustion testing.

10 C.2.4.3.4 Blanks

11 A minimum of one thermal blank will be run prior to each
12 set of three combustion test runs for a given test
13 substance composite. Each thermal blank run will be at the
14 corresponding combustion test conditions with all feeds
15 except for the test substance.
16
17

18 C.2.4.4 Process Monitoring

19 ATRS process parameters in Table C.2-2 will be monitored
20 for each combustion test at key points during the test as
21 noted in the table. Each combustion test will be a minimum
22 of 5 minutes in duration. If the duration of a combustion
23 test is greater than 15 minutes, each parameter in Table
24 C.2-2 will be recorded at least once every 15 minutes.
25
26

27 **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 Temperature-Inlet 1 will be recorded at the end of the
30 temperature ramp-up for gasification to monitor the
31 pyroprobe final temperature.
32

33 The flow rate of the exhaust gas routed to the bubblers (see
34 Section C.2.4.5.2) will be determined based on the flow
35 measurements listed in Table C.2-2.
36

C.2-9

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. CO₂ 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 CO₂. 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, composite bubbler aqueous

1 solution sample results less than method detection limit
2 (MDL) will be reported as not detected (ND), results
3 between MDL and the limit of quantitation (LOQ) will be
4 reported as not quantifiable (NQ), and numerical values
5 will not be reported.

6
7 Due to background levels of PFOA, the analytical laboratory
8 will only report numerical values for PFOA concentration in
9 the aqueous solution greater than or equal to the LOQ.
10 This is required to assure that the reported concentration
11 value is attributable to the aqueous solution sample rather
12 than to background.

13
14

15 C.2.5 Reporting of Results

16

17 C.2.5.1 Elemental Analysis Results

18

19 The results of elemental analysis for each test substance
20 composite (as noted in Section C.2.1) will be reported.
21 The laboratory reports will be included in an appendix to
22 the test report.

23

24 C.2.5.2 Combustion Stoichiometry Results

25

26 Combustion stoichiometry (as noted in Section C.2.2)
27 calculations for each test substance composite will be
28 included in an appendix to the test report.

29

30 C.2.5.3 TGA Results

31

32 The temperature for complete gasification and the TGA
33 graphical results for each test substance composite (as
34 noted in Section C.2.3) will be included in an appendix to
35 the test report.

36

37 C.2.5.4 Combustion Test Results

38

39 C.2.5.4.1 Process Monitoring

40

41 Process monitoring data (as noted in Section C.2.4.4)
42 recorded for each combustion test will be reported in
43 tabular form.

44

45 C.2.5.4.2 Exhaust Gas Monitoring

46

47 Exhaust gas O₂, CO and CO₂ monitoring results will be

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1 reported as the integrated or average value for each
2 combustion test. CO will be reported in terms of parts per
3 million by volume (ppmv). O₂ and CO₂ will be reported in
4 terms of percent by volume (%).

5
6 C.2.5.4.3 Exhaust Gas Analytical Results

7
8 Results of analyses noted in Section C.2.4.7 will be
9 reported for each combustion test.

10
11 The analytical result for each analyte in Section C.2.4.7
12 will be reported in terms of concentration (mass per
13 volume) in the bubbler aqueous solution. For each analyte,
14 this value will be used with the associated exhaust gas
15 volume to compute an exhaust gas concentration and with the
16 associated test substance mass to compute mass of analyte
17 per mass of test substance composite.

18
19 C.2.5.4.3.1 Fluoride

20
21 Fluoride ion in the exhaust gas will be reported on the
22 basis of mass of fluoride ion per mass of test substance
23 composite. The corresponding hydrogen fluoride value for
24 each will also be computed and reported for reference.

25
26 C.2.5.4.3.2 PFOA

27
28 PFOA results for the bubbler aqueous solution samples will
29 be reported as described in Section C.2.4.7.2. PFOA
30 results for associated blanks will also be reported.

31
32 If present in the bubbler aqueous solution at a
33 concentration above the matrix-specific LOQ, PFOA in the
34 exhaust gas will be reported on the basis of mass of PFOA
35 per mass of test substance composite.

36
37
38 C.2.5.5 Release Assessment

39
40 In the event that PFOA is reported for the exhaust gas
41 bubbler aqueous solution at a concentration above the LOQ
42 for the three runs for a given test substance composite,
43 then a release assessment report for the subject material
44 will be prepared following the outline in Appendix E.2.

45
46

C.2-12

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 strength of the carbon-fluorine bond:

17
18 Fluorine in organic compounds is usually determined by
19 converting organic fluorine to an inorganic fluoride.
20 Various combustion methods are routinely used for this
21 purpose. However, the carbon-fluorine bond is
22 exceptionally strong, and extremely vigorous conditions are
23 needed for a quantitative mineralization. Conventional
24 combustion conditions used for the determination of carbon
25 and hydrogen in nonfluorinated organic compounds are not
26 adequate for a quantitative analysis of fluorinated
27 surfactants.

28
29 Therefore, total fluorine analysis will be performed using
30 "extremely vigorous conditions" as described in Section
31 C.2.1.2, and the commercially available conventional
32 technique used for empirical determination of carbon and
33 hydrogen content (described in Section C.2.1.3) will
34 provide estimated values.

35
36 C.2.1.2 Total Fluorine

37
38 Each test substance composite will be characterized via
39 analysis of total fluorine content.

40
41 Based on manufacturing process knowledge, the levels of
42 total fluorine in the components of test substance
43 composites are orders of magnitude higher than the
44 potential trace level of inorganic fluoride in these
45 materials. Therefore, for this test program, the total
46 organic fluorine value for each test substance composite
47 will be considered to be the same as the total fluorine
48 value.

49

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1 Total fluorine content will be measured via the Wickbold
2 Torch method; see Appendix D.3.

3
4 C.2.1.3 Carbon and Hydrogen

5
6 In order to provide information for stoichiometric
7 calculations in Section C.2.2, the carbon and hydrogen
8 content of each test substance composite is needed. Based
9 on manufacturing process knowledge of the polymers in this
10 program, levels of sulfur, and nitrogen, ~~and oxygen~~ are
11 expected to be less than 0.1% and to thereby have
12 negligible effect on stoichiometric calculations.

13
14 C.2.1.3.1 Theoretical Determination

15
16 Where the elemental composition of a test substance
17 composite is known from the identity of the components in a
18 given composite, the carbon and hydrogen content of the
19 test substance composite can be calculated.

20
21 For example, where each of the components of a test
22 substance composite are polytetrafluoroethylene (PTFE), the
23 carbon and hydrogen can be determined knowing the molecular
24 formula for PTFE is $(C_2F_4)_n$ as follows:

25

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

26
27 C.2.1.3.2 Empirical Determination

28
29 Where compositional information on carbon and hydrogen
30 content is not known from the identity of the components in
31 a given composite, each such test substance composite will
32 be analyzed for carbon and hydrogen.

33
34 As noted in Section C.2.1.1, empirical determination of
35 carbon in test substance composites via commercially
36 available conventional techniques is expected to
37 underestimate the carbon content of the ~~sample test~~
38 substance composites due to the strength of the carbon-
39 fluorine bond. Similarly, empirical determination of
40 hydrogen in test substance composites via commercially
41 available conventional techniques is expected to
42 overestimate the hydrogen content of the ~~sample test~~
43 substance composites.

C.2-2

1
2 The carbon content of the ~~sample test~~ sample test substance composite
3 can be measured by determining the carbon dioxide (CO₂)
4 generated by the oxidation of the sample. This oxidation
5 may be accomplished by high temperature combustion,
6 catalytic combustion, or wet chemical oxidation. The CO₂ is
7 measured directly by an infrared detector or a thermal
8 conductivity detector, via absorption into a suitable
9 solution (e.g., potassium hydroxide) and gravimetric
10 determination, or by conversion to methane for measurement
11 via a flame ionization detector.

12
13 The hydrogen content of the sample can be determined by
14 difference with knowledge of the fluorine content and
15 carbon content of the sample where the moisture content and
16 chlorine content of the sample are negligible or known.
17 Alternatively, the hydrogen content of the sample is
18 measured by determining the water generated by high
19 temperature combustion of the sample. Measurement of water
20 in the combustion gas for this analysis may be accomplished
21 by techniques such as use of an infrared detector or
22 absorption on a dessicant with gravimetric determination.
23 With empirical hydrogen determination, it is important to
24 correct for the water in the combustion gas attributable to
25 the moisture content in the sample to obtain the hydrogen
26 content of the sample; see Section C.2.1.4.

27
28 Manufacturing process knowledge of the polymers will be
29 used to review the elemental analysis results and to form
30 the basis for interpreting non-detects. For example, if
31 the hydrogen analytical result for a perfluorinated polymer
32 is less than a quantitation limit of 0.1%, then the
33 analytical result will be replaced with 0.

34 35 C.2.1.4 Moisture

36
37 Where preparation (as described in Appendix A.4) for a
38 given test substance composite has involved dewatering, the
39 moisture (or solids) content of each such test substance
40 composite will be determined in order to provide a dry
41 basis for calculations as needed.

42
43 Moisture is determined by measuring the loss of weight of
44 the sample when heated under controlled conditions. A
45 representative sample is weighed and placed in a crucible
46 (or dish) and evaporated to dryness in an air or nitrogen
47 atmosphere at a defined temperature setpoint (e.g., 103 °C

C.2-3

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1 to 105 °C) in the range of 100 °C to 125 °C.
2 The moisture value is calculated as the loss in weight
3 (difference between the starting weight of sample and the
4 final weight of sample) divided by the starting weight of
5 sample. Similarly, a solids value can be calculated as the
6 final weight of sample divided by the starting weight of
7 sample.

8

9 **C.2.2 Combustion Stoichiometry**

10

11 Combustion stoichiometry calculations as described in
12 Section C.2.2 will be performed to aid in preparation for
13 combustion testing described in Section C.2.4

14

15 First, the weight percent values from Section C.2.1 are
16 converted to molar quantities on a dry basis.

17

18 Second, based on Chapter 3 of *Combustion Fundamentals for*
19 *Waste Incineration* (American Society of Mechanical
20 Engineers, 1974), the reaction products for these molar
21 quantities are calculated assuming complete combustion with
22 the following rules:

23

24 a) All carbon (C) in feed converts to carbon dioxide (CO₂)
25 $C + O_2 \rightarrow CO_2$

26

27 b) All sulfur (S) in feed converts to sulfur dioxide (SO₂)
28 $S + O_2 \rightarrow SO_2$

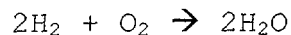
29

30 c) The halogens (Cl, F) in feed convert to hydrogen halides
31 $H_2 + Cl_2 \rightarrow 2HCl$
32 $H_2 + F_2 \rightarrow 2HF$

33

34 d) Hydrogen (H) present in feed in excess of that
35 required to yield products in item c) above will be
36 converted to water

37



38

39 e) Nitrogen (N) from feed or air is emitted as molecular
40 nitrogen

41



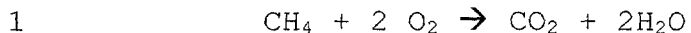
42

43 Third, with these rules, the balanced chemical reaction for
44 combustion of a compound can be written.

45

46 For example, the resulting reaction equation for a
47 hydrocarbon like methane (CH₄) is

C.2-4



2 Note that the term feed in the preceding rules (a through
3 e) includes both material being combusted and the fuel
4 source of hydrogen such as methane or methanol.
5 Additionally, stoichiometric calculations as described
6 above presume that the compounds undergoing combustion are
7 essentially free of inorganic constituents.

8
9 These calculations provide the theoretical amount of oxygen
10 needed for the overall combustion reaction for the feed
11 based on the available information used in the
12 calculations. The initial estimate for the amount of
13 oxygen to be used in combustion testing will be determined
14 from this theoretical amount with adjustments for target
15 oxygen level in thermal reactor system exhaust gas. The
16 actual amount of oxygen to be used in combustion testing
17 will be based oxygen monitoring described in Section C.2.4.

18
19 These stoichiometric calculations will also be used as
20 needed to initially estimate and adjust experimental
21 conditions for combustion testing in Section C.2.4.

22 23 **C.2.3 Thermogravimetric Analysis**

24
25 Thermogravimetric analysis (TGA) will be conducted to
26 determine the temperature range required for gasification
27 of each test substance composite. TGA will be conducted in
28 flowing air from room temperature to 1000°C as described in
29 Appendix B.1.

30
31 The TGA weight-loss profile for each test substance
32 composite will be evaluated to determine the temperature at
33 which the weight loss reaches a final asymptote across the
34 temperature range investigated. This temperature
35 corresponds to the point at which no further gasification
36 (under test conditions) occurs for the material and will be
37 considered the temperature for complete gasification of the
38 material.

39 40 **C.2.4 Combustion Testing**

41 42 **C.2.4.1 Test Objective**

43
44 The objective of the testing program described in Appendix
45 C.2 is to assess the potential for waste incineration of
46 each test substance composite to emit PFOA, based on
47 quantitative determination of potential exhaust gas levels

C.2-5

1 of PFOA from laboratory-scale combustion testing under
2 conditions representative of typical municipal waste
3 combustor operations in the U.S.

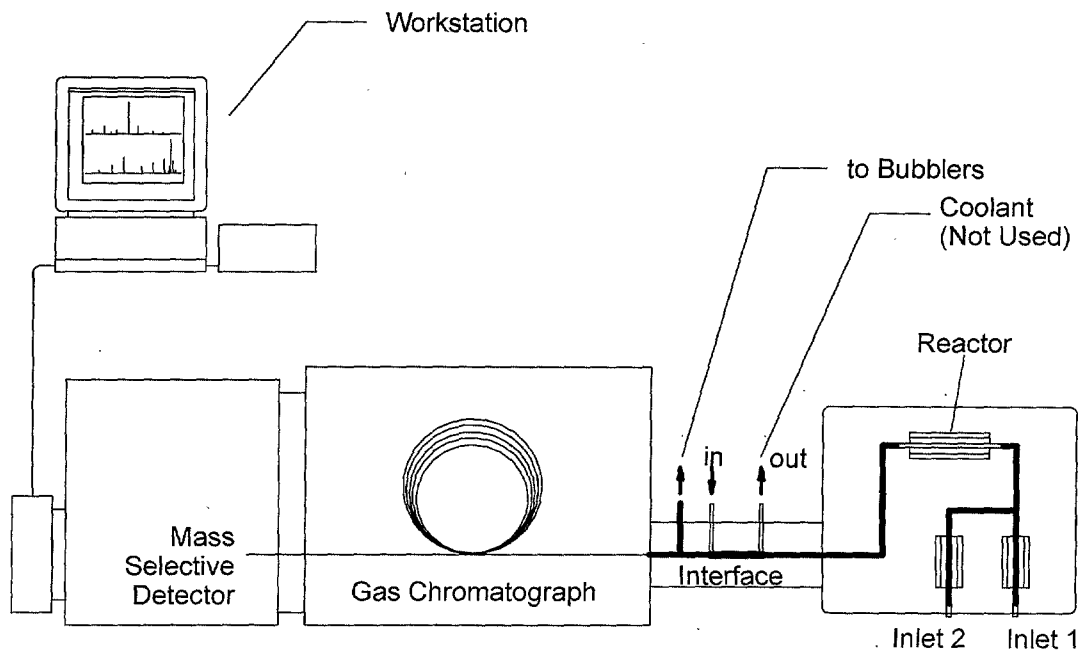
4
5 C.2.4.2 Experimental Apparatus

6
7 Combustion testing will make use of the Advanced Thermal
8 Reactor System (ATRS) at the University of Dayton Research
9 Institute (UDRI). The ATRS is a laboratory-scale, non-
10 flame, batch-charged, continuous flow thermal reactor
11 system. The use of this non-flame thermal reactor system
12 gives a conservative representation of full-scale waste
13 incineration prior to air pollution controls.

14
15 In the ATRS, the test sample is gasified and transported to
16 a high temperature reactor. In the high temperature
17 reactor, the sample vapors are subjected to controlled
18 conditions for residence time and temperature. As
19 described in Sections C.2.4.5 and C.2.4.6, combustion
20 products will be monitored or collected for quantitative
21 analysis.

22
23 A schematic of the ATRS as configured for this test program
24 is shown in Figure C.2-1.

25
26 **Figure C.2-1. Schematic of ATRS for this Test Program**



27
28 The ATRS consists of a reactor assembly and in-line gas

1 chromatograph/detector system connected via an interface.
2 The reactor assembly consists of a thermally insulated
3 enclosure housing the sample introduction, reactor, and
4 transfer line systems.

5
6 Sample introduction for solid materials (Inlet 1) employs a
7 pyroprobe, a device designed to gasify samples by heating
8 them at a fixed rate. The main gas flow will also be fed
9 via Inlet 1, and Inlet 2 will be used to feed supplemental
10 flow.

11
12 During combustion tests, the transfer line between the
13 pyroprobe and the reactor is heated and maintained above
14 200 °C. The reactor is housed within its own small tube
15 furnace and may be independently heated to as high as 1100
16 °C. (Actual conditions for this test program are presented
17 in Section C.2.4.3.) The transfer line from the reactor to
18 the interface is heat traced to greater than 200 °C to
19 prevent cool regions where reactor products could otherwise
20 be lost through condensation.

21
22 The interface routes the combustion exhaust gas to the in-
23 line gas chromatograph (GC) and mass selective detector
24 (MSD) or to sample collection for off-line analysis. For
25 combustion testing in this test program, the interface will
26 also be maintained above 200 °C. Exhaust gas monitoring for
27 this program is described in Section C.2.4.5.

28 29 C.2.4.3 Combustion Test Experimental Conditions

30
31 Each test substance composite will be subjected to
32 laboratory-scale incineration using the experimental
33 apparatus described in Section C.2.4.2.

34 35 C.2.4.3.1 Combustion Air

36
37 Synthetic air (mixture of 21% oxygen and 79% nitrogen) will
38 be used in place of compressed air to prevent potential
39 interference in the experimental system due to background
40 levels of CO₂ in compressed air.

41 42 C.2.4.3.2 Fuel

43
44 Methanol will be used, as needed, as a supplemental fuel to
45 ensure the presence of sufficient hydrogen to convert
46 fluorine to hydrogen fluoride (HF) and chlorine to hydrogen
47 chloride (HCl).

C.2-7

1
2 As noted in *Municipal Solid Waste in the United States:*
3 *2000 Facts and Figures* (EPA, 2002), paper and paper
4 products (made from wood) make up the largest component of
5 municipal solid waste (MSW). The sum of paper and paper
6 products with wood in MSW makes up over 30% of MSW.

7
8 During the 19th century, methanol was produced from wood and
9 was known as wood alcohol. Therefore, methanol can be used
10 in this experimental program as a surrogate for the paper
11 and wood fraction of MSW.

12 13 C.2.4.3.3 Operating Conditions

14
15 The target operating conditions for the high temperature
16 reactor during the combustion tests for each test substance
17 composite identified in Appendix A.3 are presented in Table
18 C.2-1.

19
20 **Table C.2-1. Combustion Test Target Operating Conditions**

Temperature	1000 °C
Residence Time	2 sec
O ₂ concentration in exhaust gas	10%
H ₂ O concentration in exhaust gas	1415%
Number of replicate runs	3

21
22 These conditions are conservatively representative of
23 typical furnace operating conditions of municipal waste
24 combustors (MWCs) and of typical secondary chamber
25 operating temperatures for medical waste incinerators in
26 the U.S. See Appendix D.4 for supporting information.

27
28 Temperature and residence time values in Table C.2-2 will
29 be fixed setpoints for these experiments. The temperature
30 of the high temperature reactor will be controlled within
31 +10 °C to assure isothermal operation.

32
33 ~~The amount of ATRS sample size for each~~ the test substance
34 ~~composites fed to the ATRS~~ in this testing program will be
35 a measured amount less than 5 mg. The actual amount
36 ~~fed sample size~~, gasification rate (determined from TGA),
37 air supply, and fuel supply will be adjusted to assure that
38 the oxygen level in the exhaust will be greater than or
39 equal to the concentration in Table C.2-1 throughout each
40 test to be representative of typical MWC conditions. The
41 fuel supply and air supply will also be adjusted as needed
42 to approach the target H₂O concentration in exhaust gas in

C.2-8

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1 Table C.2-1.

2

3 The pyroprobe section final temperature (at end of
4 temperature ramp-up) will be 750 °C or as needed to assure
5 this section is 50 to 100 °C above the highest temperature
6 for complete gasification across the test substance
7 composites as determined from the TGA resultexperiments;
8 see Section C.2.3. This is necessary to assure complete
9 gasification of the sample of test substance composite and
10 a common set of experimental conditions across the test
11 materials during combustion testing.

12

13 C.2.4.3.4 Blanks

14

15 A minimum of one thermal blank will be run prior to each
16 set of three combustion test runs for a given test
17 substance composite. Each thermal blank run will be at the
18 corresponding combustion test conditions with all feeds
19 except for the test substance.

20

21 C.2.4.4 Process Monitoring

22

23 ATRS process parameters in Table C.2-2 will be monitored
24 for each combustion test at key points during the test as
25 noted in the table. Each combustion test will be a minimum
26 of 5 minutes in duration. If the duration of a combustion
27 test is greater than 15 minutes, each parameter in Table
28 C.2-2 will be recorded at least once every 15 minutes.

29

30 **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

31

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

35

36 The flow rate of the exhaust gas routed to the bubblers (see

C.2-9

1 Section C.2.4.5.2) will be determined based on the flow
2 measurements listed in Table C.2-2.

3
4 The amount of material fed to the system will be verified
5 by weighing the pyroprobe insert cartridge before and after
6 each experiment.

7
8 Exhaust gas monitoring is described in Section C.2.4.5.

9
10 C.2.4.5 Exhaust Gas Monitoring

11
12 Combustion exhaust gas will be continuously monitored for
13 oxygen during each combustion test via in-line MSD or via
14 an oxygen monitor. CO₂ in exhaust gas will be monitored via
15 in-line GC, in-line MSD, or a continuous monitor; or
16 exhaust gas will be collected in Tedlar® bags for off-line
17 analysis of CO₂. Carbon monoxide (CO) in exhaust gas will
18 be monitored via in-line GC or a continuous monitor; or
19 exhaust gas will be collected in Tedlar® bags for off-line
20 analysis of CO. Tedlar® bag samples may be collected at
21 the exit of the bubblers described in Section C.2.4.6.

22
23 C.2.4.6 Exhaust Gas Sampling

24
25 Gas samples for off-line analysis will be collected as
26 described in Appendix D.1.

27
28 A minimum of 60 mL of bubbler aqueous solution composite is
29 expected from each combustion test. Of this, a minimum of
30 45 mL will be directed to PFOA analysis, and the remainder
31 will be directed to fluoride ion analysis.

32
33 C.2.4.7 Exhaust Gas Analysis

34
35 C.2.4.7.1 Fluoride Ion

36
37 A portion of the composite bubbler aqueous solution sample
38 from each combustion test collected as described in Section
39 C.2.4.6 will be analyzed for fluoride ion via ion
40 chromatography.

41
42 C.2.4.7.2 PFOA

43
44 A portion of the composite bubbler aqueous solution sample
45 from each combustion test collected as described in Section
46 C.2.4.6 will be analyzed for PFOA via LC/MS/MS as described
47 in Appendix D.2.

1
2 As described in Appendix D.2, composite bubbler aqueous
3 solution sample results less than method detection limit
4 (MDL) will be reported as not detected (ND), ~~sample results~~
5 between MDL and the limit of quantitation (LOQ) will be
6 reported as not quantifiable (NQ), and numerical values
7 will not be reported ~~for such samples~~.

8
9 Due to background levels of PFOA, the analytical laboratory
10 will only report numerical values for PFOA concentration in
11 the aqueous solution greater than or equal to the LOQ.
12 This is required to assure that the reported concentration
13 value is attributable to the aqueous solution sample rather
14 than to background.

15
16 ~~C.2.4.8 Test Substance Sampling & Analysis~~

17
18 ~~See Section C.2.1. (Elemental Analysis)~~

19
20 C.2.5 Reporting of Results

21
22 C.2.5.1 Elemental Analysis Results

23
24 The results of elemental analysis ~~of~~ for the each test
25 substance composites (as noted in Section C.2.1) will be
26 reported. The laboratory reports will be included in an
27 appendix to the test report.

28
29 C.2.5.2 Combustion Stoichiometry Results

30
31 Combustion stoichiometry (as noted in Section C.2.2)
32 calculations for each test substance composite will be
33 included in an appendix to the test report.

34
35 C.2.5.3 TGA Results

36
37 The temperature for complete gasification and the TGA
38 graphical results for each test substance composites (as
39 noted in Section C.2.3) will be included in an appendix to
40 the test report.

41
42 C.2.5.4 Combustion Test Results

43
44 C.2.5.4.1 Process Monitoring

45
46 Process monitoring data (as noted in Section C.2.4.4)
47 recorded for each combustion test will be reported in

C.2-11

1 tabular form.

2

3 C.2.5.4.2 Exhaust Gas Monitoring

4

5 Exhaust gas O₂, CO and CO₂ monitoring results will be
6 reported as the integrated or average value for each
7 combustion test. CO will be reported in terms of parts per
8 million by volume (ppmv). O₂ and CO₂ will be reported in
9 terms of percent by volume (%).

10

11 C.2.5.4.3 Exhaust Gas Analytical Results

12

13 Results of analyses noted in Section C.2.4.7.2 will be
14 reported for each combustion test.

15

16 The analytical result for each analyte in Section
17 C.2.4.7.2 will be reported in terms of concentration (mass
18 per volume) in the bubbler aqueous solution. For each
19 analyte, this value will be used with the associated
20 exhaust gas volume to compute an exhaust gas concentration
21 and with the associated test substance mass to compute mass
22 of analyte per mass of test substance composite.

23

24 C.2.5.4.3.1 Fluoride

25

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

30

31 C.2.5.4.3.2 PFOA

32

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

36

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

41

42 ~~C.2.5.5 Test Substance Results~~

43

44 ~~Elemental compositions will be reported as indicated in~~
45 ~~Section C.2.4.6.1 above.~~

46

47 C.2.5.6 5 Release Assessment

C.2-12

1
2 In the event that PFOA is ~~found in~~ reported for the exhaust
3 gas bubbler aqueous solution at a concentration above the
4 LOQ for the three runs for a given test substance
5 composite, then the potential for release from full-scale
6 municipal and/or medical waste incineration (including
7 application of air pollution controls) of the subject
8 material in the U.S. will be assessed to inform the basis
9 for possible next steps. a release assessment report for the
10 subject material will be prepared following the outline in
11 Appendix E.2.

12
13 ~~This assessment will consider a number of factors such as~~
14
15 ~~□ PFOA results from this testing program reported per~~
16 ~~Section C.2.5.4.3.2,~~
17 ~~□ Estimated concentration of subject material in feed to~~
18 ~~applicable type(s) of full-scale waste incinerators (based~~
19 ~~on such information as Appendix A.2, supplemental~~
20 ~~information on material applications, and available~~
21 ~~information on hydrogen fluoride concentration in waste~~
22 ~~incinerator exhaust as upper bound), and~~
23 ~~□ Use and abatement effectiveness of common post-combustion~~
24 ~~air pollution control equipment (e.g., lime scrubbing,~~
25 ~~carbon adsorption) employed by typical operating full-scale~~
26 ~~waste incinerators.~~
27
28 ~~See Appendix E.2 for the draft outline of the Release~~
29 ~~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 bubbler (which is empty) will be added to the
20 front end of this series of bubblers to serve as a knock-out
21 pot if calculations or preliminary measurements indicate
22 that 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 tubing;
30 this rinsate will be combined with the bubbler composite
31 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).

D.1-1

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 C₁₈ 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 C₁₈ 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 less than the

D.2-1

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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 PFOA anion 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	<ul style="list-style-type: none"> 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 C₁₈ 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 C₁₈ SPE cartridge described in section 4.4 of the method (e.g., methanol).
3.3 Note at top of page 8	<ul style="list-style-type: none"> 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,	<ul style="list-style-type: none"> The following text will be used in place of Note 1 with respect to the PFOA analysis

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Note 1	<p>conducted for this testing program:</p> <p>In order to avoid contamination, the use of disposable labware (tubes, pipets, etc.) is required.</p>
3.3 Notes, Note 4	<ul style="list-style-type: none"> The following text will be used in place of Note 4 with respect to the PFOA analysis conducted for this testing program: <p>Solvents (e.g., methanol) used for this analysis must be checked for the presence of contaminants by LC/MS/MS before use.</p>
3.5 opening text prior to 3.5.1	<ul style="list-style-type: none"> 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	<ul style="list-style-type: none"> 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 C₁₈ 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	<ul style="list-style-type: none"> 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	<ul style="list-style-type: none"> Extraction using the C₁₈ 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

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	(e.g., methanol) samples.
4.4, item 1	<ul style="list-style-type: none"> 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	<ul style="list-style-type: none"> 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	<ul style="list-style-type: none"> 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	<ul style="list-style-type: none"> 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
3
4
5
6
7

D.2.5 Reference

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

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1 **APPENDIX D.3**
2 **WICKBOLD TORCH METHOD FOR TOTAL FLUORINE**

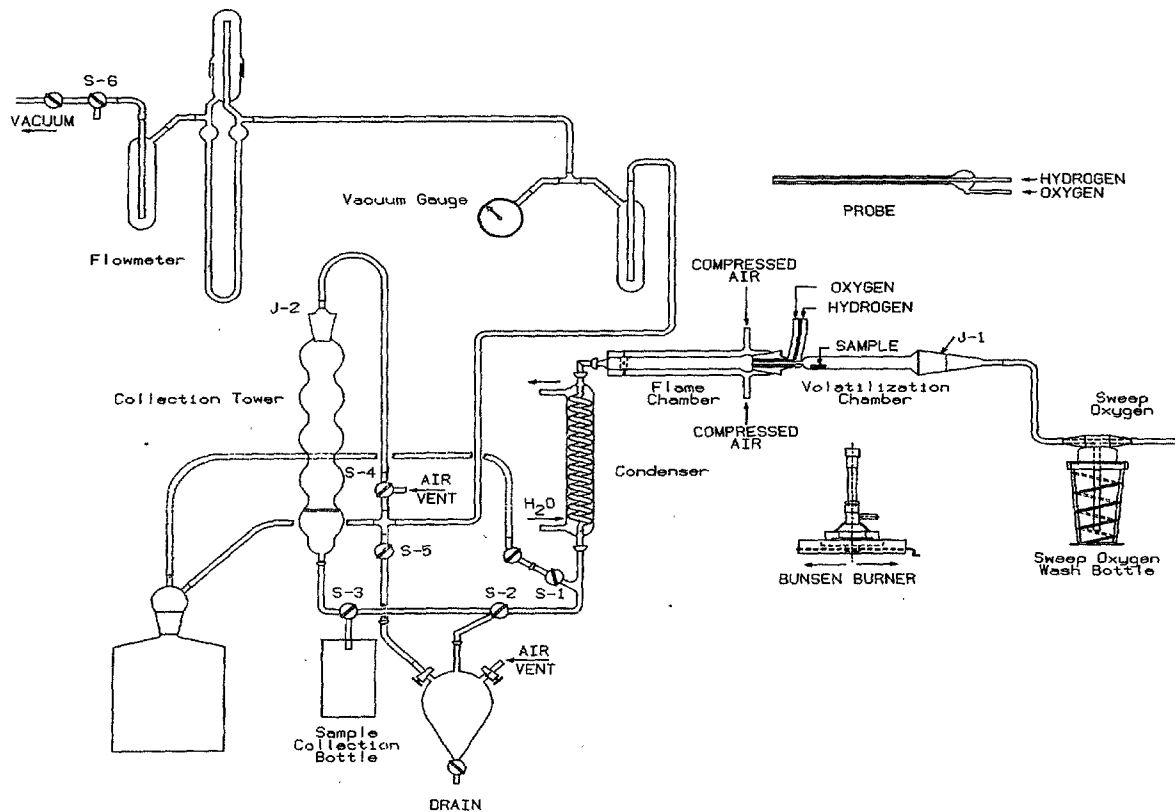
3
4 D.3.1 Introduction

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**



D.3-1

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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 is assured by the
30 use of specialized equipment with shielding and elaborate
31 safety devices by well-trained personnel at a qualified
32 laboratory.

33

34 D.3.5 References

35

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

40

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

Appendix D.4 Waste Incineration and Operation Conditions

Polymers of the sort being investigated in this testing program may be present at trace to low concentrations in the feedstreams to municipal waste combustors and/or medical waste incinerators in the U.S.

D.4.1 Types of Incinerators

D.4.2.1 Municipal Waste Combustors

According to the Integrated Waste Services Association (IWSA), there are a total of 98 waste-to-energy facilities operating municipal waste combustors (MWCs) in the U.S. as of 2002. (IWSA 2002) Table D.4-1 summarizes the number and annual capacity of these units by type of technology employed.

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%

D.4.1.2 Hospital/Medical/Infectious Waste Incinerators

Although earlier reports indicated approximately 2400 medical waste incinerators in the U.S. in the 1990s burning approximately 846 thousand tons of hospital and medical/infectious waste (EPA 1997), the current EPA Office of Air Quality, Planning, and Standards (OAQPS) inventory indicates that there are 116 hospital/medical/infectious waste incinerators (HMIWIs) in the U.S. as of July 28, 2003. (EPA 2003)

This represents a greater than 90% reduction in the number of operating HMIWIs in the U.S. Many medical waste incinerators were closed rather than upgraded to meet new emission standards, as hospitals improved their programs to segregate infectious ("red bag") waste burned in HMIWIs from non-infectious ("black bag") waste handled as municipal solid waste after it leaves the hospital. Consequently, the amount of segregated infectious waste

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burned in HMIWIs is expected to be less than 0.3 million tons per year.

EPA notes that over 97% of medical waste incinerators are controlled air modular units (EPA 2000a). Recent communication with EPA OAQPS indicates that virtually all existing HMIWIs are controlled air modular (two-chamber) units.

D.4.2 Incinerator Operating Conditions

Many incinerators for municipal solid waste are designed to operate in the combustion zone at 1800 °F (982 °C) to 2000 °F (1093 °C) to ensure good combustion. (EPA 1995) EPA new source performance standards (NSPS) and emission guidelines for both municipal waste combustors (MWCs) and hospital/medical/infectious waste incinerators (HMIWIs) are based on the use of "good combustion practices" (GCP). (EPA 1997, EPA 2000b, EPA 2000c, Van Remmen 1998)

Referring to MWCs, Donnelly notes, "Design of modern efficient combustors is such that there is adequate turbulence in the flue gas to ensure good mixing, a high-temperature zone (greater than 1000 °C) to complete burnout, and long enough residence time at high temperature (1-2 sec) for complete burnout." (Donnelly 2000) The term "flue gas" here refers to the gas above the grate.

With respect to HMIWIs, Van Remmen states "any unit which presently [prior to compliance date] has a [secondary chamber] residence time less than two seconds at 1000 °C does not meet the requirement for good combustion under the new regulations." (Van Remmen 1998)

Similarly, most MWCs operate with a 2 second gas residence time in the high temperature zone in order to assure compliance with emission standards on carbon monoxide (CO) and dioxins.

D.4.2.1 MWC Operating Conditions

D.4.2.1.1 Mass Burn MWC

Review of the IWSA Directory (IWSA 2002) indicates that almost all of these mass burn units are mass burn water wall furnaces. Nearly all mass burn water wall furnaces

have reciprocating grates or roller grates to move the waste through the combustion chamber. (EPA 1996a)

Studies on the Millbury, Massachusetts mass burn water wall MWC produced gas temperature versus residence time results. (Scavuzzo, Strempek, and Strach 1990) Calculations based on Figure 6 of this paper indicate a time-averaged temperature of 2238 °F (1226 °C) across 2 seconds. The corresponding gas temperature at the 2 second level from this figure is 1750 °F (954 °C).

A report on the Warren County, New Jersey mass burn water wall MWC indicates that the design gas temperature between the grate and secondary air inject was greater than 2000 °F (1093 °C) over a gas residence time of an additional 2.2 seconds. (Scheuetzenduebel and Nobles 1990) This report also shows that this MWC was designed for 2 seconds residence time above 1800 °F (982 °C) between the introduction of secondary air and the exit of the furnace section. (Scheuetzenduebel and Nobles 1990) The temperature profile (Figure 21) in the temperature correlation test report (Scheuetzenduebel 1989) for this MWC shows the full load gas temperature at the secondary air injection point is 2650 °F, and the gas temperature at the 2-second point is 1850 °F. Therefore, testing indicates an average temperature of 2250 °F (1232 °C) over this 2 second gas residence time for the Warren County unit. A related report for the Warren County MWC by the design firm indicates that the exhaust gas oxygen concentration is nominally 10%. (Blount Energy Corporation 1989)

Information from these 2 MWCs demonstrates that the average gas temperature across a 2 second residence time for mass burn MWCs is conservatively expected to be greater than 1100 °C.

Test report data from a typical mass burn MWC (Fairfax, Virginia) indicates typical average furnace exit gas concentrations are 10.8% oxygen (dry basis) and 18.4% moisture (water). (Clean Air Engineering, 1997)

As indicated in Table D.4.1, mass burn units account for over 76% of the municipal solid waste incinerated in the U.S.

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D.4.2.1.2 RDF MWC

Furnace temperatures as well as flue gas oxygen and moisture (H₂O) levels for Mid-Connecticut RDF combustor performance tests operating under good combustion conditions across a range of steam loads (Finklestein and Klicius 1994) are summarized in Table D.4-2.

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

The average operating conditions for this RDF unit across the range of steam loads are 1016 °C, 8.4% O₂, and 14.1% moisture.

Examination of the report and MWC temperature monitoring practices indicates that these temperatures are effectively combustion zone exit temperatures. Therefore, in order to determine the average MWC combustion zone temperature across a 2 second gas residence time, it is necessary to understand the time-temperature profile of the MWC.

Since waste combustion in this and most other RDF units in the U.S. involves burning on the grate (EPA 1996a) similar to the operation of mass burn MWCs, the time-temperature profile in an RDF unit is expected to be similar to that described in Section D.4.2.1.1 above. Based on this similarity and the temperatures in Table D.4-2, the average gas temperature across a 2 second residence time for RDF units is conservatively expected to be greater than 1100 °C.

As indicated in Table D.4.1, RDF units account for approximately 22% of the municipal solid waste incinerated in the U.S.

D.4.2.1.1 Modular MWC

Modular MWCs are generally small dual-chamber units, accounting for less than a total of 2% of the municipal solid waste incinerated in the U.S. in 2002. Modular MWCs

are generally equipped with auxiliary fuel burners in the secondary chamber. (EPA 1996a) EPA notes that the secondary chamber exit temperature of modular MWCs is maintained at typically 980 to 1200 °C. (EPA 1996a)

A typical modular MWC in Polk County, Minnesota is operated with secondary chamber gas residence time of 2 seconds, secondary chamber exit temperature in the range of 1800 °F (982 °C) to 2000 °F (1093 °C), flue gas oxygen concentrations in the range of 10% to 13%, and flue gas moisture in the range of 10% to 15% (Pace Analytical 2003).

Based on first principles, the secondary chamber exit temperature is expected to be the minimum gas-phase temperature for the chamber. Therefore, secondary chamber average gas temperatures for modular MWCs are expected to be 1000 °C or greater.

As indicated in section D.4.1, such modular units are generally small MWCs and account for less than a total of 2% of the municipal solid waste incinerated in the U.S.

D.4.2.1.4 MWC Summary

Considering the relative quantities of municipal waste burned annually in each type of MWC and the data in this section, typical operating conditions for the high temperature zone of most MWCs are >1000 °C average temperature across 2 second residence time with exit gas concentrations of 10% O₂ and >15% moisture.

D.4.2.2 HMIWI Operating Conditions

The range of temperatures for the secondary chamber of controlled air medical waste incinerators has been reported as 980 to 1200 °C. (Theodore 1990) EPA notes that auxiliary fuel (e.g., natural gas) is burned in the secondary chamber of medical waste incinerators to sustain temperatures in the range of 985 to 1095 °C and that combustion air at 100 to 300 % in excess of the stoichiometric requirement is usually added to the secondary chamber. (EPA 2000a)

In its model plant description background document, EPA notes that the average moisture content in HMIWI flue gas was about 10 % based on available data, and EPA states "limited data show that older [HMIWI] units typically have residence times that range from essentially 0 seconds up to

about 1 second." (EPA 1994b) However, as noted above, a more recent report indicates that HMIWIs still in operation have secondary chamber temperatures greater than or equal to 1000 °C with a gas residence of 2 seconds. (Van Remmen 1998) For example, EPA studied the incinerator at Weeks Hospital in New Hampshire as a typical HMIWI with a design residence time of 2 seconds in the secondary chamber. (EPA 1996b) During this testing, the average exit secondary chamber exit temperature was 1024 °C, and the flue gas oxygen concentration was 13.5%. (EPA 1996b)

Review of test reports for all HMIWIs in the EPA docket for the HMIWI NSPS and EG rulemakings that are listed in EPA's current HMIWI inventory (EPA 2003) does not refute Van Remmen's statement above on residence time and temperature and indicates HMIWI flue gas oxygen concentrations for these units in the range of 10 to 15% and stack moisture concentrations as high as 30% (after wet scrubbing). (Environmental Laboratories Inc. 1993, EPA 1996, HDR Engineering 1994a, HDR Engineering 1994b, METCO Environmental 1992, Technical Services, Inc. 1993, Technical Services, Inc. 1994a, Technical Services, Inc. 1994b) Apparently, the older HMIWIs referred to in EPA's model plant description background document either have been shut down or upgraded to operate with secondary chamber exit temperatures higher than 1000 °C with gas residence time of 2 seconds.

Secondary chamber temperature of HMIWIs is monitored near the secondary chamber outlet. (EPA 1994) Hence, when the auxiliary burner (located on the end opposite from the outlet) is in use, the average gas temperature in an HMIWI secondary chamber is greater than the outlet temperatures noted above. Therefore, secondary chamber average gas temperatures for HMIWIs are expected to be 1000 °C or greater with a gas residence time of 2 seconds.

In summary, typical operating conditions for the secondary chamber of operating HMIWIs in the U.S. are 1000 °C average temperature across 2 second residence time with exit gas concentrations of 13% O₂ and 10% moisture.

D.4.3 Pollution Control Equipment

Over 99% of large MWC capacity operates with a spray dryer absorber/scrubber. (IWSA 2003) Approximately 80% of large MWC capacity operates using carbon injection as part of the

pollution control system. (IWSA 2003) Due to requirements in the NSPS (EPA 2000b) and EG (EPA 200c) for small MWCs, small MWCs planning continued operation are generally upgrading or have upgraded their pollution control equipment to add spray dryer absorbers or other acid gas control and carbon injection.

Review of EPA's HMIWI inventory (EPA 2003) indicates that essentially all HMIWIs have some form of wet or dry scrubbing for acid gas control.

D.4.4 Summary

Approximately 30 million tons per year of municipal solid waste is combusted in the United States annually in waste-to-energy municipal waste combustors in 2003. Approximately 0.3 million tons per year of segregated medical waste is combusted annually in the United States in hospital/medical/infectious waste incinerators in 2003. Considering the relative amounts of waste combusted annually, typical operating conditions for waste incineration in the U.S. across these two classes of units are as follows:

Average Temperature	>1000 °C
Residence Time	2 sec
O ₂ concentration in exhaust gas	10%
H ₂ O concentration in exhaust gas	15%

EPA emission regulations currently in place or in place by 2005 that operating municipal waste combustors and hospital/medical/infectious waste incinerators typically have or will have air pollution control equipment such as wet or dry scrubbing for acid gas control.

References

Blount Energy Corporation. Correlation Procedure for Continuously Monitoring Furnace Temperatures (Warren County Resource Recovery Facility), March 22, 1989.

Clean Air Engineering. Test Report for Covanta of Fairfax, Inc. I-95 Energy/Resource Recovery Facility, 1997.

Donnelly, J.R. Waste Incineration Sources: Municipal Waste Combustion. In: W.T., ed., Air Pollution Engineering Manual, 2nd edition. Air and Waste Management Association. New York, NY: Van Nostrand Reinhold, 2000, pp 257-268.

Environmental Laboratories Inc. Stack Test Report for Emissions Testing of the Bethesda Memorial Hospital Waste Incinerator, Boynton Beach Florida, September 13, 1993.

Environmental Protection Agency (EPA). Municipal Waste Combustion Assessment: Technical Basis for Good Combustion Practice, EPA 600/8-89-063, August 1989.

EPA. Medical Waste Incinerators-Background Information for Proposed Standards and Guidelines: Control Technology Performance Report for New and Existing Facilities, EPA-453/R-94-044a, July 1994.

EPA. Medical Waste Incinerators - Background Information for Proposed Standards and Guidelines: Model Plant Description and Cost Report for New and Existing Facilities, EPA-453/R-94-045a, July 1994.

EPA. Decision Maker's Guide to Solid Waste Management, Volume II, Chapter 8, 1995.

EPA. AP-42, Fifth Edition, Volume I, Chapter 2: Solid Waste Disposal, Section 2.1, Refuse Combustion, Supplement B, October 1996.

EPA. Medical Waste Incineration Emission Test Report: Weeks Memorial Hospital, Lancaster, New Hampshire, EMC Report 96-MWI-11, March 1996.

EPA. Standards of Performance for New Stationary Sources and Emission Guidelines for Existing Sources: Hospital/Medical/Infectious Waste Incinerators, 62 Federal Register 48346, September 15, 1997.

D.4-8

DRAFT/SUBJECT TO REVISION
DOES NOT REFLECT INPUT FROM ALL MEMBER COMPANIES

EPA. Exposure and Human Health Reassessment of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) and Related Compounds, Part I: Estimating Exposure to Dioxin-Like Compounds Volume 2: Sources of Dioxin-Like Compounds in the United States, Chapter 3, EPA/600/P-00/001Bb, Draft Final Report, September 2000.

EPA. New Source Performance Standards for New Small Municipal Waste Combustion Units, 65 Federal Register 76350, December 6, 2000.

EPA. Emission Guidelines for Existing Small Municipal Waste Combustion Units, 65 Federal Register 76378, December 6, 2000.

EPA. HMIWI Facility and Emissions Inventory, draft, July 28, 2003,
www.epa.gov/ttnatw01/129/hmiwi/2003hmiwi_inventory.xls

Finklestein, A. and R. D. Klicius. National Incinerator Testing and Evaluation Program: The Environmental Characterization of Refuse-derived Fuel (RDF) Combustion Technology, Mid-Connecticut Facility, Hartford, Connecticut, EPA-600/R-94-140 (NTIS PB96-153432), December 1994.

HDR Engineering. Performance Test Results Report Submittal: Incinerator Waste Management Facility, Mayo Foundation, Rochester, Minnesota, June 7, 1994.

HDR Engineering. Performance Test Results Report Supplemental Submittal Charts, Data Sheets, Operator Log, CEMS Data: Incinerator Waste Management Facility, Mayo Foundation, Rochester, Minnesota, June 10, 1994.

Integrated Waste Services Association (IWSA). The 2002 IWSA Directory of Waste-to-Energy Plants, 2002,
www.wte.org/2002_directory/IWSA_2002_Directory.html

IWSA. Air Pollution Control Devices on Operating Waste-to-Energy Plants: Year 2002, 2003.

METCO Environmental. Source Emissions Survey of University of Texas Medical Branch, Incinerator Number 2 Exhaust Duct, Galveston, Texas, TACB Permit C-18655 for Clever Brooks, July 1992.

D.4-9

DRAFT/SUBJECT TO REVISION
DOES NOT REFLECT INPUT FROM ALL MEMBER COMPANIES

Midwest Research Institute. Updated Hospital/Medical/ Infectious Waste Incinerator Inventories Received from Various Regions, States, and Counties, January 27, 1999.

Pace Analytical. Comprehensive Emissions Test Report: MSW Incinerator Unit No. 1 ESP Outlet & MSW Incinerator Unit No. 2 ESP Outlet (Polk County Solid Waste Plant), March 11-14, 2003.

Scavuzzo, S. A., J. R. Strempek, and L. Strach. "The Determination of the Thermal Operating Characteristics in the Furnace of a Refuse-Fired Power Boiler" in Proceedings of the 1990 National Waste Processing Conference, American Society of Mechanical Engineers (ASME), 1990, pp. 397-404.

Schuetzenduebel, W. G. and W. C. Nobles. "New Jersey's First Resource Recovery Facility (The Warren County Energy Recovery Facility)" in Proceedings of the 1990 National Waste Processing Conference, ASME, 1990, pp. 321-343.

Schuetzenduebel, W. G. Blount Energy Corporation Report - Furnace/Boiler Temperature Correlation: Warren County Resource Recovery Facility, Oxford, New Jersey, October 1989.

Technical Services, Inc. Source Test Report: Boca Raton Hospital, Boca Raton, Florida, March 31-April 2, 1993.

Technical Services, Inc. Source Test Report: Mercy Hospital South Miami, Florida, July 27-28, 1994.

Technical Services, Inc. Source Test Report: St. Vincent's Medical Center Jacksonville, Florida, August 30, 1994.

Theodore, L. Air Pollution Control and Waste Incineration for Hospitals and Other Medical Facilities, Van Nostrand Reinhold, New York, 1990, pp 313-320.

Van Remmen, T. Evaluation of the available air pollution control technologies for achievement of the MACT requirements in the newly implemented new source performance standards (NSPS) and emission guidelines (EG) for hospital and medical/infectious waste incinerators, Waste Management, 1998, Vol. 18, pp 393-402.

D.4-10

DRAFT/SUBJECT TO REVISION
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1 APPENDIX E.2**2 OUTLINE FOR RELEASE ASSESSMENT REPORT**

3
4 If triggered by Appendix C.2.5.5 of this ECA, then the
5 potential for release from full-scale municipal and/or
6 medical waste incineration, as applicable, (including
7 application of air pollution controls) of the subject
8 material in the United States will be assessed to put the
9 data into perspective. At a minimum, the report will
10 follow the general outline described below and will state
11 assumptions, document the basis for the assumptions made,
12 quantitatively estimate the variability of calculated
13 estimates (based on the variability of the parameters in
14 the evaluation), and qualitatively discuss the uncertainty
15 of calculated estimates.

16 1.0 Introduction

- 17
18
- 19 • Statement of objective for combustion testing of
20 test substance composites.
21
 - 22 • Applicability of the laboratory-scale combustion
23 testing to full-scale municipal waste combustors
24 (MWCs) and/or medical waste incinerators (as
25 applicable) in the United States.
26

27 2.0 Summary of study results

- 28
- 29 • A listing of exhaust gas analytical results reported
30 for each test condition.
31
 - 32 • A listing of test substance composite analytical
33 results reported for each test condition.
34

35 3.0 Discussion

- 36
- 37 • Description of the combustion section of the
38 applicable waste incineration process(es) being
39 evaluated (MWC and/or medical waste incinerator)
40 including the rationale for selecting test target
41 temperature(s) and description of typical
42 operational parameters. Cross-reference to or
43 submission of relevant parts of Appendix D.4 of this
44 ECA can satisfy this provision.
45

E.2-1

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

6 **4.0 Extrapolation of laboratory test results to the**
7 **typical waste incineration process(es), as applicable,**
8 **described in Section 3.0 (above) for each test**
9 **substance composite to be evaluated.**

- 10
11 • The relevance of the subject test substance
12 composite to MWCs and/or medical waste incinerators.
13
14 • The estimated concentration of the subject test
15 substance composite to the applicable type(s) of
16 waste incinerator. Available information on
17 hydrogen fluoride concentration in waste incinerator
18 exhaust can provide the basis for an upper bound on
19 this estimated concentration.
20
21 • A description of the extrapolation.
22
23 • A description of any assumptions used.
24
25 • Any unique qualitative or quantitative descriptors
26 of the test, the testing equipment, and the results
27 deemed necessary for informative review of the test
28 and test results.
29

30 **5.0 Sensitivity Analysis**

- 31
32 • Assessment of the impact of variability
33 (quantitative) and uncertainty (qualitative) in each
34 parameter on the evaluation results.
35

36 **6.0 Conclusions**

37
38 **7.0 References**
39
40

**APPENDIX G
INCINERATION TESTING ECA QUALITY ASSURANCE PROJECT PLAN: OUTLINE & PLANNED CONTENT**

Section	Planned Sections	Primary Guidance for Preparing Each QAPP Section (ref: EPA QAMS-005/80)	Supplemental Guidance Reference for Preparing Each QAPP Section (ref: EPA QA/R-5 QAPP Guidance elements)	Required Content of Incineration Testing ECA
not numbered	Title Page	1.0 Title Page with Provision for Approval Signatures	A1 Title and Approval Sheet A2 Distribution List	to be included in QAPP
not numbered	Table of Contents	2.0 Table of Contents	A2 Table of Contents	to be included in QAPP
1.0	Introduction	not applicable	not applicable	to be satisfied by cross-reference to introductory text in ECA and Appendices, as applicable
2.0	Project Description	3.0 Project Description	A5 Problem Definition/Background A6 Project/Task Description B1 Sampling Process Design (Experimental Design)	to be satisfied by cross-reference to ECA (Parts I, IV) and Appendix C.1 or C.2, as applicable
3.0	Project Organization and Responsibility	4.0 Project Organization and Responsibility	A4 Project/Task Organization	to be included in QAPP
4.0	Quality Assurance Objectives	5.0 Quality Assurance Objectives for Measurement Data	A7 Quality Objectives and Criteria	to be included in QAPP

5.0	Sampling Procedures	6.0 Sampling Procedures	B2 Sampling Methods	to be satisfied by cross-reference to Appendix C.1 or C.2 (as applicable) and to Appendix D.1
6.0	Sample Handling and Custody	7.0 Sample Custody	B3 Sample Handling and Custody	to be included in QAPP
7.0	Analytical Methods	9.0 Analytical Methods	B4 Analytical Methods	to be satisfied by cross-reference to Appendices C.2, D.2, and D.3, as applicable
8.0	Calibration Procedures and Frequency	8.0 Calibration Procedures and Frequency	B7 Instrument/Equipment Calibration and Frequency	to be included in QAPP in summary form for chemical analysis equipment
9.0	Internal Quality Control Checks	11.0 Internal Quality Control Checks and Frequency	B5 Quality Control	to be included in QAPP consistent with ECA Appendices, as applicable
10.0	Data Reduction, Validation, and Reporting	10.0 Data Reduction, Validation, and Reporting	D1 Data Review, Verification, and Validation	to be included in QAPP consistent with Appendices C.1, C.2, and D.2, as applicable
11.0	Preventive Maintenance	13.0 Preventive Maintenance	B6 Instrument/Equipment Testing, Inspection, and Maintenance	to be included in QAPP in summary form for chemical analysis equipment
12.0	Accuracy, Precision, Completeness	14.0 Procedures to Assess Data Precision,	not applicable	to be included in QAPP

13.0	Performance and System Audits	Accuracy, and Completeness 12.0 Performance and System Audits	not applicable	to be included in QAPP as applicable; not applicable to laboratory(ies) performing analysis pursuant to 40 CFR 792
14.0	Corrective Actions	15.0 Corrective Actions	C1 Assessments and Response Actions	to be included in QAPP as applicable; not applicable to laboratory(ies) performing analysis pursuant to 40 CFR 792
15.0	Quality Assurance Reports to Management	16.0 Quality Assurance Reports to Management	C2 Reports to Management	to be included in QAPP as applicable; not applicable to laboratory(ies) performing analysis pursuant to 40 CFR 792