



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

10/24/03 01:54 PM

To: Rich Leukroth/DC/USEPA/US@EPA
cc:
Subject: revised draft fluoropolymer ECA testing program document

Rich,

Attached is the revised draft fluoropolymer incineration ECA testing program document as revised based on drafting committee discussions through the end of our October 22 drafting committee conference call.

(See attached file: FP Incin Test Program draft 10-24-03.pdf)

As discussed, I have done my best to address all comments made by the drafting committee, and in some cases have left a placeholder in brackets in italics for such placeholder to note where further work is in progress.

I think I have correctly captured all the revisions as discussed. I have also corrected typos (e.g., "in a rubber mill" to "on a rubber mill"), made minor formatting changes to get reasonable page breaks (using extra blank lines), and tried to improve conformance between the text in section IV of the shell document and the footnotes to Table 1 (while I was making revision to section IV to conform with requested revisions in Appendix B).

Also, as we discussed and per the timing we discussed, I understand that you will assure distribution of this document to the work groups today (presumably via Mary D.) on behalf of the drafting committee.

As previously agreed, Table 1 continues to have TBDs in it.

As my earlier note indicated, there has not been sufficient time since Wednesday's call to reformat Appendix A.

I understand that information has been or soon will be submitted to EPA indicating that polyethylene, polypropylene, and glass containers are all suitable for use in this testing program.

I look forward to our further work in the drafting committee. If you have any questions, please let me know.

Best Regards,

Robert Giraud

This communication is for use by the intended recipient and contains information that may be privileged, confidential or copyrighted under applicable law. If you are not the intended recipient, you are hereby formally notified that any use, copying or distribution of this e-mail, in whole or in part, is strictly prohibited. Please notify the sender by return e-mail and delete this e-mail from your system. Unless explicitly and conspicuously designated as "E-Contract Intended", this e-mail does not constitute a contract offer, a contract amendment, or an acceptance of a contract offer. This e-mail does not constitute a consent to the use of sender's contact information for direct marketing purposes or for transfers of data to third parties.

Francais Deutsch Italiano Espanol Portugues Japanese Chinese Korean

http://www.DuPont.com/corp/email_disclaimer.html



FP Incin Test Program draft 10-24-03.

1 **Fluoropolymers Incineration Testing Program**

2 DRAFT 10-24-03

3
4
5 **I. CHEMICAL SUBJECT TO THE ECA**

6 The test substances being studied in this testing program
7 are identified in Appendix A. The basis for test substance
8 selection and the preparation of the composites to undergo
9 testing are also described in Appendix A.

10
11 **II. PURPOSE OF TESTING PROGRAM**

12 The purpose of this testing program is to investigate
13 incineration of designated test substances under
14 laboratory-scale conditions representative of typical
15 municipal waste combustor operations in the U.S. to
16 quantitatively determine potential emission levels of PFOA.

17
18 **III. SCOPE OF TESTING PROGRAM**

19 The testing program will consist of

- 20
21 1) conducting the testing listed in Table 1 in accordance
22 with the test standards specified in Table 1 for the
23 test substances identified in Appendix A and
24
25 2) submitting the reports specified in Table 1 in
26 accordance with the deadlines set forth in Table 1.

27
28 **IV. DESCRIPTION OF TESTING PROGRAM**

29 The testing program has 2 phases as follows: Phase I PFOA
30 Transport Testing and Phase II Incineration Testing.

31
32 **A. Phase I PFOA Transport Testing**

33 This testing is described in Appendix B and determines the
34 PFOA transport efficiency across the laboratory-scale
35 thermal reactor system. Phase I testing provides the
36 necessary foundation for Phase II testing.

37
38 Following completion of Phase I and prior to initiation of
39 Phase II, the Test Sponsor will provide a letter report to
40 EPA with the result for the overall recovery across the
41 laboratory-scale thermal reactor system determined from
42 Phase I testing.

43
44 If this overall recovery for either PFOA or total fluorine
45 is greater than or equal to 70%, the Test Sponsor will
46 proceed to Phase II testing.

1 If this overall recovery for both PFOA and total fluorine
2 is less than 70%, then a Technical Consultation between the
3 Agency and the Test Sponsor will be held to reach agreement
4 on whether Phase II testing should proceed and, if so, on
5 what (if any) revisions to the plans, test standards, and
6 schedule for Phase II testing to adopt.

7
8 If this consultation does not result in an agreement to
9 proceed with Phase II testing, a more complete test report
10 for Phase I will be submitted to EPA within 60 days of
11 completion of the Technical Consultation.

12
13 If Phase II testing is conducted, a more complete test
14 report for Phase I will be included in the later Phase II
15 Test Report rather than in a separate report.

16
17 B. Phase II Incineration Testing

18 As described in Section IV.A, Phase II testing may be
19 conducted depending on the result of Phase I testing or the
20 Technical Consultation.

21
22 Phase II testing is described in Appendix C.
23
24

1 **Table 1. Required Testing, Test Standards, and Reporting**

Phase I PFOA Transport Testing	Test Standard	Deadline for Final Report ^{1,3}
Transport Efficiency	See Appendix B	TBD

2

Phase II Incineration Testing for Test Substance Composites	Test Standard	Deadline for Final Report ^{2,4,6}
Elemental Analysis ⁵	ASTM D3176 or equivalent as described in Appendix C.1	TBD
Combustion Stoichiometry ⁵	See Appendix C.2	TBD
Thermogravimetric Analysis ⁵	ASTM E1868 as annotated in Appendix C.3	TBD
Laboratory-scale Combustion Testing ⁵	See Appendix C.4 - C.6	TBD
Release Assessment	See Appendix C.6	TBD

3

4 1 Number of months after the effective date of the Order that
5 incorporates this ECA when final report for this testing is due.
6 Following completion of Phase I and prior to initiation of Phase II,
7 the Test Sponsor will provide a letter report to EPA with the result
8 for the overall recovery across the laboratory-scale thermal reactor
9 system determined from Phase I testing.

10 2 If the overall recovery result from Phase I testing is less than
11 70% for both PFOA and total fluorine, then a Technical Consultation
12 will be held to reach agreement on whether Phase II testing should
13 proceed and, if so, on what (if any) revisions to adopt to the plans,
14 test standards, and schedule for Phase II. If such agreement is not
15 reached, Phase II testing is not required under the Order that
16 incorporates this ECA.

17 3 A more complete test report for Phase I testing will be submitted
18 within 60 days of the completion of the Technical Consultation if this
19 consultation does not result in an agreement to proceed with Phase II
20 testing. A more complete test report for this testing will be included
21 in the Phase II test report if Phase II testing is conducted.

22 4 Number of months after initiation of Phase II testing period when
23 final report for this testing is due. Phase II testing period will be
24 initiated following Technical Consultation agreement to conduct Phase
25 II testing or after completion of Phase I testing, whichever is later.

26 5 The results of this testing will be provided in the final report
27 for Phase II.

28 6 A release assessment will be included in the final report for
29 Phase II if quantifiable levels of PFOA are found in the exhaust gas
30 from Phase II combustion testing.

1

2 **APPENDICES**

3

4 A. Test Substances

5

6 B. PFOA Transport Testing

7

8 C. Incineration Testing

APPENDIX A. TEST SUBSTANCES

1. Identification

The four composite test substances for this test program will be prepared from the fluoropolymers identified in the March 14, 2003 Letter of Intent (LOI) submitted by the Society of the Plastics Industry on behalf of the four LOI signatories (as corrected). The specific fluoropolymer types (with CAS numbers and associated monomers) going into each of the four composite test substances (grouped as shown) are presented in Table A-1 below. Each fluoropolymer used in each relevant test substance composite will have been made using APFO.

Table A-1. Test Substance Composites by Type and CAS Number

Test Substance	Fluoropolymer Type	CAS Number	Associated Monomers
Composite 1 - PTFE resin (dry non-melt)	PTFE	9002-84-0	TFE
Composite 2 - Dry melt resins	FEP	25067-11-2	TFE, HFP
	PFA	26655-00-5	TFE, PPVE
		31784-04-0	TFE, PEVE
	THV	25190-89-0	TFE, HFP, VDF
	ETFE	68258-85-5	TFE, E
Composite 3 - Fluoroelastomers Copolymers (dry non-melt)	HTE	35560-16-8	TFE, HFP, E
	Fluoroelastomer Copolymers	9011-17-0	VDF, HFP
	Fluoroelastomer Terpolymers	25190-89-0	TFE, HFP, VDF
	Base resistant elastomers	54675-89-7,	TFE, VDF, P
		27029-05-6	TFE, P
	Perfluoroelastomers	26425-79-6	TFE, PMVE
CTFE elastomers	9010-75-7	CTFE, VDF	
Low temperature elastomers	CBI	TFE, VDF	
Composite 4 - Aqueous Dispersions	PTFE	9002-84-0	TFE
	FEP	25067-11-2	TFE, HFP
	PFA	26655-00-5	TFE, PPVE
		31784-04-0	TFE, PEVE
THV	25190-89-0	TFE, HFP, VDF	

1 Confidential business information (CBI) regarding the
2 chemical identity of Low temperature elastomers has
3 previously been submitted to EPA under separate cover.

4 5 2. Selection

6 Review of Figure A-1 demonstrates that fluoropolymers
7 industry products can be divided into 3 broad categories
8 representative classes as follows:

- 9
- 10 • Dry melt resins
 - 11 • Dry non-melt resins and gums
 - 12 • Aqueous dispersions

13
14 These three broad categories can in turn be divided into
15 four representative classes as follows:

- 16
- 17 • Dry melt resins
 - 18 1. FEP, PFA, THV, ETFE, HTE
 - 19
 - 20 • Dry non-melt resins and gums
 - 21 2. PTFE resin
 - 22 3. Fluoroelastomer gums
 - 23
 - 24 • Aqueous dispersions
 - 25 4. PTFE, FEP, PFA, THV
 - 26

27 Composite samples of each of these four representative
28 classes were selected as the test substance for this
29 testing program in order to represent the entire range of
30 fluoropolymers involved.

31 32 3. Preparation of Fluoropolymer Composites

33 34 3.1 Approach

35
36 A composite mixture of representative fluoropolymers, as
37 solids, will be prepared for each of the four test
38 substance composites identified in Table A-1.

39
40 The polymer samples will be first quality product polymer,
41 substantially free of inorganic constituents. Each sample
42 will be from a representative grade for each applicable
43 fluoropolymer type from each applicable company.

44
45 A hypothetical example for Composite Z in Table A-2 below
46 shows how the composites will be assembled. In this

1 example with 4 types across 4 companies, there are 11 x's.
2 Hence, composite Z would be made up of 11 equal proportions
3 of the materials indicated with an x.

4
5

Table A-2. Example for Compositing Across Companies & Types

Test Substance	Fluoropolymer Type	Company A	Company B	Company C	Company D
Composite Z	Type 1		x	x	x
	Type 2	x	x	x	x
	Type 3			x	
	Type 4	x	x	x	

6

7 For Composite 1 - PTFE resin (where there is a single
8 fluoropolymer type), a representative sample of PTFE resin
9 from each company producing PTFE resin will be mixed
10 together in equal proportions across applicable companies
11 to form the Composite 1 - PTFE resin.

12

13 3.2 Preparation

14

15 Representative samples of each component from each
16 applicable company for each composite will be sent to the
17 laboratory(ies) in packaging customarily used for product
18 sample packaging or in polyethylene, polypropylene, or
19 glass containers.

20

21 Each composite will be prepared under laboratory conditions
22 designed to prevent cross-contamination and designed to
23 assure solids temperatures less than or equal to 60 °C.

24

25 Following preparation of each composite, the composite will
26 be placed in a polyethylene, polypropylene, or glass
27 container.

28

29 3.2.1 Composite 1

30

31 PTFE resin is available in powder form. Equal weights of
32 PTFE resin powder samples across applicable companies will
33 be mixed together in dry form to yield Composite 1.

34

35 3.2.2 Composite 2

36

37 FEP, PFA, THV, ETFE, and HTE dry melt resins are available
38 in pellet form. Each component of Composite 2 will be
39 size-reduced (e.g., ground) to produce powder. Equal
40 weights of the powder form of each component (following the

1 approach in the example for Composite Z in Section 3.1)
2 will be mixed together in dry form to yield Composite 2.

3
4 A sample of polyethylene pellets will be size-reduced using
5 the same technique and equipment to provide a blank. The
6 resulting polyethylene powder will be archived.

7
8 *[text on size reduction blank under further development]*

9
10 3.2.3 Composite 3

11
12 Fluoroelastomers are available in slab, lump, or sheet
13 form. Composite 3 will be prepared following one of the
14 following approaches:

15
16 a) Equal weights of each component (following the approach
17 in example for Composite Z in Section 3.1) will be mixed
18 on a rubber mill to produce a homogenous slab of preset
19 thickness to yield Composite 3.

20
21 Or

22
23 b) Each component of Composite 3 will be cyrogenically
24 cooled (to make the elastomers brittle) and size-reduced
25 (e.g., ground) to produce powder. Equal weights of the
26 powder form of each component (following the approach in
27 the example for Composite Z in Section 3.1) will be mixed
28 together in dry form to yield Composite 3.

29
30 A sample of non-fluorinated synthetic rubber will be size-
31 reduced using the same technique and equipment to provide a
32 blank. The resulting non-fluorinated rubber sample will be
33 archived.

34
35 *[text on size reduction blank under further development]*

36
37 3.2.4 Composite 4

38
39 Aqueous dispersions of PTFE, FEP, PFA, and THV are
40 available as dispersions containing 20 to 60% fluoropolymer
41 solids by weight. Composite 4 will be prepared following
42 one of the following approaches:

43
44 a) Equal weights (on a dry solids basis) of each component
45 in aqueous dispersion form (following the approach in
46 example for Composite Z in Section 3.1) will be mixed
47 together in liquid form. Solids will be separated from

1 the resulting liquid composite to yield low water content
2 (i.e., drip free) fine solids.

3

4 Or

5

6 b) Solids will be separated from liquid for each component
7 of Composite 4 to yield low water content (i.e., drip
8 free) fine solids for each component. Equal weights of
9 the solids form of each component (following the approach
10 in the example for Composite Z in Section 3.1) will be
11 mixed together to yield Composite 4.

12

13 3.3 Verification

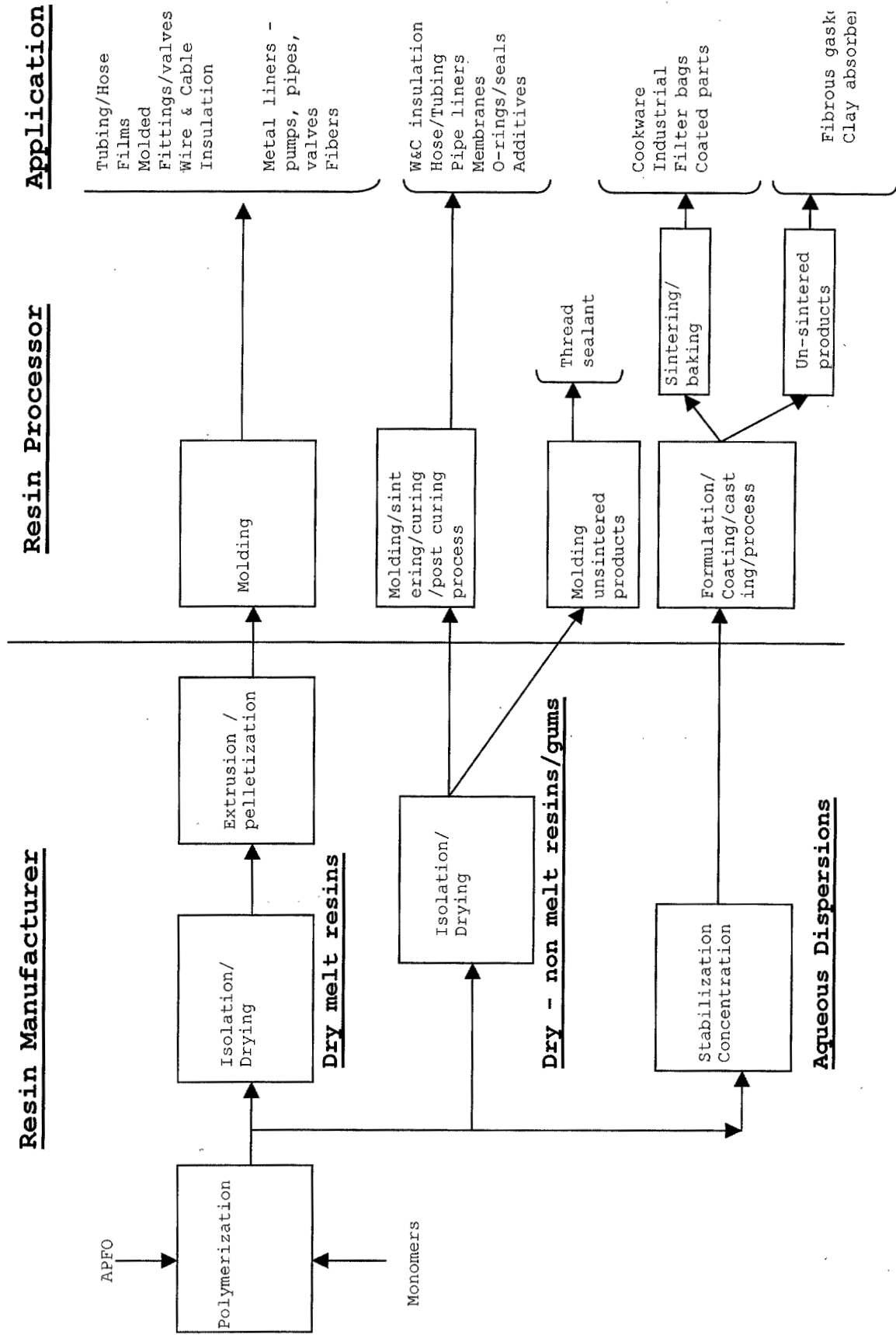
14

15 In order to assure that composite samples in this testing
16 program have been made up of clearly identified materials,
17 the preparation of the composites will include formal Chain
18 of Custody procedures. A chain of custody form will be
19 included with each component material going into the
20 composite to show the identity of the component material
21 and each transfer of custody from its point of origination
22 to preparation of the composite. For documentation, the
23 laboratory preparing a given composite will generate a
24 report to be submitted to EPA as CBI along with a sanitized
25 version for the public record from which CBI has been
26 removed.

27

28 Once prepared, each composite will be accompanied by a new
29 chain of custody until it reaches the incineration testing
30 facility.

Figure A-1. Fluoropolymer Industry Overview



1 **APPENDIX B. PFOA TRANSPORT TESTING**

2
3 PFOA Transport Efficiency

4 Quantitative transport of PFOA across the laboratory-scale
5 thermal reactor system described in Appendix C will be
6 verified. A PFOA standard of known purity greater than or
7 equal to 97% will be used for this testing. For these
8 transport tests, 0.5 to 5 mg of PFOA will be gasified at
9 150 to 250 °C (based on thermogravimetric analysis of PFOA)
10 with transfer line and reactor temperatures 0 to 100 °C
11 higher than the gasification temperature. Sampling and
12 analysis will be performed to determine quantitation of
13 PFOA and fluorine in corresponding laboratory-scale thermal
14 reactor system exhaust gas samples.

15
16 The amount of PFOA and fluorine determined in this exhaust
17 gas sample will be compared to the amount of PFOA (as PFOA
18 and as fluorine) fed to the thermal reactor system. The
19 amount of PFOA fed to the system will be verified by
20 weighing the pyroprobe insert cartridge before and after
21 each experiment. The amount of fluorine fed to the system
22 will be known from the amount of PFOA fed, the purity of
23 the PFOA, and the known fluorine fraction of the PFOA
24 standard.

25
26 If the resulting transport efficiency for either PFOA or
27 total fluorine is greater than or equal to 70%, then the
28 overall recovery across the thermal reactor system is also
29 greater than or equal to 70%.

30
31 If the resulting transport efficiency for both PFOA and
32 total fluorine is less than 70%, then flexible tubing
33 between the thermal reactor system and the sample
34 collection apparatus and/or the high temperature reactor
35 will be examined for PFOA and/or total fluorine. If the
36 flexible tubing is examined, it will either be extracted
37 using methanol with the methanol extract being analyzed for
38 PFOA and total fluorine, or a portion of the tubing will be
39 directly subjected to total fluorine analysis. If the
40 reactor is examined, the reactor will be removed from the
41 system and extracted with methanol, and the solvent sample
42 will be analyzed for PFOA and total fluorine.

43
44 In this case, the overall recovery across the experimental
45 system will be determined. The amount of the analyte (PFOA
46 or total fluorine as applicable) from examination of the
47 tubing and/or the reactor will be added to the amount of

1 analyte determined in the exhaust gas sample for comparison
2 with the amount of analyte fed to the thermal reactor
3 system to determine the overall recovery across the
4 experimental system.

5
6 The thermal reactor system apparatus in this testing
7 program is configured such that additional extractions of
8 the transfer lines between the pyroprobe and the reactor
9 and between the reactor and the vent line (to which the
10 flexible tubing is connected) are not feasible.

11
12 Three replicate transport efficiency test runs will be
13 conducted. A minimum of one blank run will be conducted
14 prior to each transport efficiency test run.

15
16 Exhaust gas sampling and analysis for PFOA and total
17 fluorine are described in Appendix C, Section 5.3.

1 **APPENDIX C. INCINERATION TESTING**

2
3 The standards for preliminary testing are described in
4 Sections 1, 2, and 3 below. The standard for combustion
5 testing is presented in Section 4. Section 5 describes the
6 standard for sampling and analysis for the combustion
7 testing. Section 6 outlines how results of this testing
8 program will be reported.

9

10 1. Elemental Analysis

11 Each test substance composite will undergo elemental
12 analysis to provide data for stoichiometric calculations.

13

14 Ultimate analysis (ASTM D3176) is a standard practice for
15 analysis of coal and coke. It is used to determine carbon
16 and hydrogen in a material via analysis of the gaseous
17 products of its complete combustion; to determine sulfur,
18 nitrogen, and ash in the material; and to calculate oxygen
19 in the material by difference.

20

21 Table C-1 presents the reference standards for test methods
22 for determination of carbon, hydrogen, nitrogen, sulfur,
23 chlorine, ash, moisture, and oxygen for the test substance
24 composites in this program and includes ASTM test methods
25 referred to in ASTM D3176.

26

27 **Table C-1. Reference Standards**

Parameter	Test Method
Carbon	ASTM D3178, ASTM D5373, or equivalent
Hydrogen	ASTM D3178, ASTM D5373, or equivalent
Nitrogen	ASTM D3179, ASTM D5373, or equivalent
Sulfur	ASTM D3177, ASTM D4239, or equivalent
Chlorine	Bomb combustion (EPA 5050 or ASTM D808)/chloride ion analysis (ion chromatography or ion selective electrode), ASTM D2361, ASTM D46610B, or equivalent
Ash	ASTM D3174, ASTM D5142, ASTM D482, or equivalent
Moisture	ASTM D3173, ASTM D5142, or equivalent
Oxygen	By difference per ASTM D3176

28

29 The reference standards will be adapted, as needed, to
30 elemental analysis of the test substance composites in this
31 testing program. Preparation steps for coal and coke noted
32 in the ASTM standard test methods in Table C-1 are not
33 required for application of these methods to the test
34 substance composites. The sample sizes in the test methods

1 in Table C-1 will be adjusted as necessary in this testing
2 program based on available amount of composite sample.

3
4 In accordance with ASTM D3176, oxygen will be determined by
5 difference (i.e, the difference between 100% and the sum of
6 the other measurements). If fluorine concentration is
7 analyzed at a different laboratory from that used for the
8 other elemental analyses, the calculated oxygen level in
9 the material will be adjusted downward to account for
10 fluorine.

11
12 Fluorine (total fluorine) content will be determined via
13 Wickbold Torch; see Attachment C-1. Based on manufacturing
14 process knowledge, the levels of total fluorine in the
15 components of test substance composites are orders of
16 magnitude higher than the potential trace level of
17 inorganic fluoride in these materials. Therefore, for this
18 test program, the total organic fluorine value for each
19 test substance composite will be assumed to be the same as
20 the total fluorine value.

21
22 Manufacturing process knowledge of the polymers will be
23 used to review the elemental analysis results and to form
24 the basis for interpreting non-detects. For example, if
25 the elemental analysis result for a non-chlorinated or ash-
26 free polymer is less than a quantitation or detection limit
27 of 0.1%, then the analytical result will be replaced with
28 0.

29
30 Additionally, ASTM D3176 will be used, as necessary, as a
31 reference to convert elemental analysis results to a basis
32 (e.g., dry) other than on which the results are reported by
33 the elemental analysis laboratory.

34 35 36 2. Combustion Stoichiometry

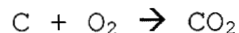
37 The results of the elemental analysis will form the basis
38 for combustion stoichiometry calculations needed to help
39 establish combustion test conditions.

40
41 First, the weight percent values from elemental analysis
42 (see Section 1) are converted to molar quantities.

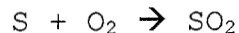
43
44 Second, based on Chapter 3 of Combustion Fundamentals for
45 Waste Incineration (American Society of Mechanical
46 Engineers, 1974), the reaction products for these molar
47 quantities are calculated assuming complete combustion with

1 the following rules:

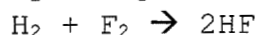
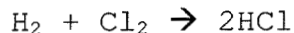
2
3 a) All carbon (C) in feed converts to carbon dioxide (CO₂)



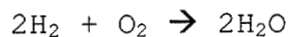
5
6 b) All sulfur (S) in feed converts to sulfur dioxide (SO₂)



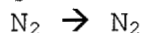
8
9 c) The halogens (Cl, F) in feed convert to hydrogen halides



12
13 d) Hydrogen (H) present in feed in excess of that
14 required to yield products in item c) above will be
15 converted to water

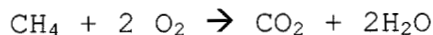


17
18 e) Nitrogen (N) from feed or air is emitted as molecular
19 nitrogen



21
22 Third, with these rules, the balanced chemical reaction for
23 combustion of a compound can be written.

24
25 For example, the resulting reaction equation for a
26 hydrocarbon like methane (CH₄) is



29
30 Note that the term feed in the preceding rules (a through
31 e) includes both material being combusted and the fuel
32 source of hydrogen such as methane or methanol.

33 Additionally, stoichiometric calculations as described
34 above presume that the compounds undergoing combustion are
35 essentially free of inorganic constituents.

36
37 The amount of oxygen needed for the overall combustion
38 reaction for a feed is called the stoichiometric oxygen
39 level. The actual oxygen level for combustion is generally
40 set in terms of excess oxygen or excess air.

41
42 Additional stoichiometric calculations will be performed as
43 needed to set and adjust experimental conditions for
44 combustion testing; see Section 4.3.

1 3. Thermogravimetric Analysis

2 Thermogravimetric analysis (TGA) will be conducted to
3 determine the temperature range required for gasification
4 of each test substance composite. TGA will be conducted in
5 flowing air from room temperature to 1000°C at 25°C/minute
6 using 1 to 5 mg samples. ASTM E1868 as annotated will be
7 used as the guideline for this analysis; see Attachment C-
8 3.

9
10 The TGA weight-loss profile for each test substance
11 composite will be evaluated to determine the temperature at
12 which the weight loss reaches a final asymptote across the
13 temperature range investigated. This temperature
14 corresponds to the point at which no further gasification
15 (under test conditions) occurs for the material and will be
16 considered the temperature for complete gasification of the
17 material. See Section 4.3.

18
19
20 4. Combustion Testing

21
22 4.1 Test Objective

23
24 The objective of this combustion testing program is to
25 investigate incineration of each test substance composite
26 under laboratory-scale conditions representative of typical
27 municipal waste combustor operations in the U.S. to
28 quantitatively determine potential emission levels of PFOA.
29

30 4.2 Experimental Apparatus

31
32 Combustion testing will make use of the Advanced Thermal
33 Reactor System (ATRS) at the University of Dayton Research
34 Institute (UDRI). The ATRS is a laboratory-scale, non-
35 flame, batch-charged, continuous flow thermal reactor
36 system. The use of a non-flame thermal reactor system
37 gives a conservative representation of full-scale waste
38 incineration.

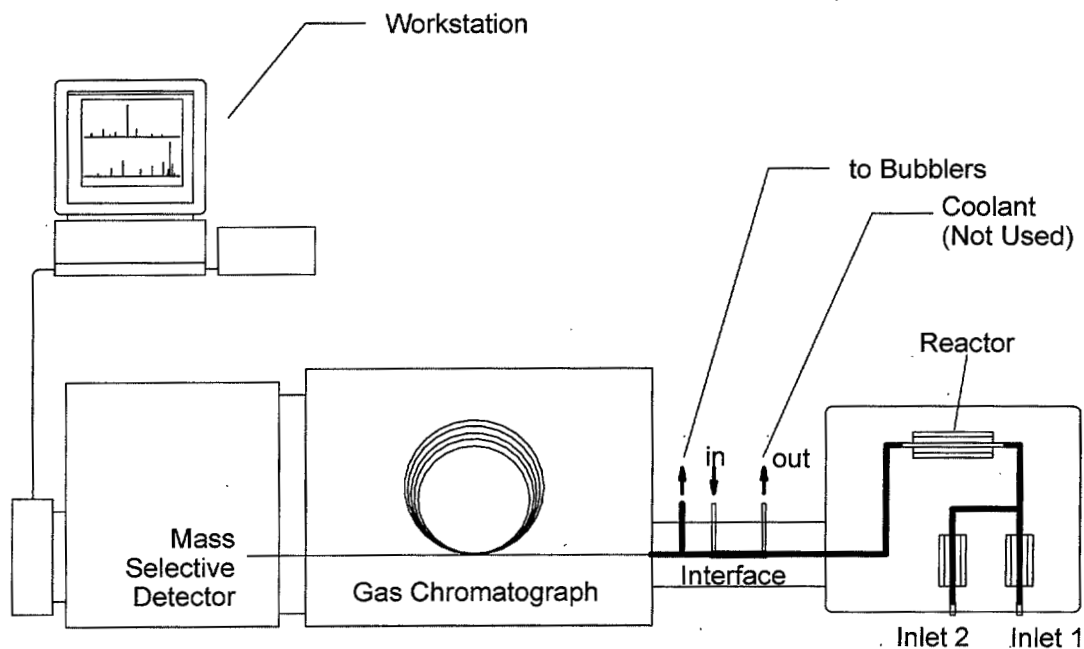
39
40 In the ATRS, the test sample is gasified and transported to
41 a high temperature fused silica reactor. In the high
42 temperature reactor, the sample vapors are subjected to
43 controlled conditions of residence time, temperature, and
44 excess air. Combustion products (section 5) will be
45 collected for quantitative analysis.

46
47 A schematic of the ATRS as configured for this test program

1 is shown in Figure C-1.

2

3 **Figure C-1. Schematic of ATRS for this Test Program**



4

5

6 The ATRS consists of a reactor assembly and in-line gas
7 chromatograph/detector system connected via an interface.
8 The reactor assembly consists of a thermally insulated
9 enclosure housing the sample introduction, reactor, and
10 transfer line systems.

11

12 Sample introduction for solid materials (Inlet 1) employs a
13 pyroprobe, a device designed to gasify samples by heating
14 them at a fixed rate. The main gas flow will also be fed
15 via Inlet 1, and Inlet 2 will be used to feed supplemental
16 flow.

17

18 During combustion tests, the transfer line between the
19 pyroprobe and the reactor is heated and maintained above
20 200 °C. The reactor is housed within its own small tube
21 furnace and may be independently heated to as high as 1200
22 °C. (Actual conditions for this test program are presented
23 in Section 4.3.) The transfer line from the reactor to the
24 interface is heat traced to greater than 200 °C to prevent
25 cool regions where reactor products could otherwise be lost
26 through condensation.

27

28 The interface routes the combustion exhaust gas to the in-

1 line gas chromatograph (GC) and mass selective detector
2 (MSD) or to sample collection for off-line analysis. For
3 combustion testing in this test program, the interface will
4 also be maintained above 200 °C.

5
6 Exhaust gas sampling and analysis (including use of the in-
7 line GC and MSD) are described in Section 5.

8 9 4.3 Combustion Test Experimental Conditions

10
11 Each test substance composite will be subjected to
12 laboratory-scale incineration using the experimental
13 apparatus described in Section 4.2.

14 15 4.3.1 Combustion Air

16
17 Synthetic air (mixture of 21% oxygen and 79% nitrogen) will
18 be used in place of compressed air to prevent potential
19 interference in the experimental system due to background
20 levels of CO₂ in compressed air.

21 22 4.3.2 Fuel

23
24 Methanol will be used, as needed, as a supplemental fuel to
25 ensure the presence of sufficient hydrogen to convert
26 fluorine to hydrogen fluoride (HF) and chlorine to hydrogen
27 chloride (HCl).

28
29 As noted in *Municipal Solid Waste in the United States:*
30 *2000 Facts and Figures* (EPA, 2002), paper and paper
31 products (made from wood) make up the largest component of
32 municipal solid waste (MSW). The sum of paper and paper
33 products with wood in MSW makes up over 30% of MSW.

34
35 During the 19th century, methanol was produced from wood and
36 was known as wood alcohol. Therefore, methanol can be used
37 in this experimental program as a surrogate for the paper
38 and wood fraction of MSW.

39 40 4.3.3 Operating Conditions

41
42 The target operating conditions for the high temperature
43 reactor during the combustion tests are presented in Table
44 C-2.

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

Test Material	Composite 1 - PTFE resin	Composite 2 - Dry melt resin	Composite 3 - Fluoroelastomer	Composite 4- Aqueous dispersion
Temperature	900 °C	900 °C	900 °C	900 °C
Residence Time	2 sec	2 sec	2 sec	2 sec
O ₂ conc. in Exhaust Gas	10%	10%	10%	10%
H ₂ O conc. in Exhaust Gas	14%	14%	14%	14%
Number of replicate runs	3	3	3	3

2
3 These conditions are representative of typical operating
4 conditions for the high temperature zone of municipal waste
5 combustors (MWCs) in the U.S. The temperature was selected
6 to conservatively represent the low end of normal MWC
7 operating temperatures and is also less than typical
8 secondary chamber operating temperatures for medical waste
9 incinerators in the U.S. See Attachment C-4 for supporting
10 information.

11
12 The expected sample size is in the range of 1 to 3 mg. The
13 actual sample size, the gasification rate (determined from
14 TGA), and the excess air will be adjusted to assure that
15 the oxygen level in the exhaust will be greater than or
16 equal to the concentration in Table C-2 to be
17 representative of typical MWC conditions.

18
19 Temperature and residence time values in Table C-2 will be
20 fixed setpoints for the experiment. Fuel supply and excess
21 air will be adjusted as needed to approach the H₂O
22 concentration target in Table C-2. Excess air will be
23 further adjusted as needed based on fuel supply. Note that
24 O₂ and H₂O exhaust gas concentration values will be
25 determined by calculation in planning the experiment.

26
27 The temperature in the pyroprobe section will be maintained
28 at 750 °C or as needed to assure this section is 50 to 100
29 °C above the highest temperature for complete gasification
30 across the test materials as determined from the TGA
31 experiments; see Section 3. This is necessary to assure
32 complete gasification of the sample of test material and a
33 common set of experimental conditions across the test

1 materials during combustion testing.

2

3 4.4 Blanks

4

5 A minimum of one thermal blank will be run prior to each
6 set of three combustion test runs. Each thermal blank run
7 will be at the corresponding combustion test condition
8 except without the test material.

9

10 4.5 Process Monitoring

11

12 ATRS process parameters in Table C-3 will be monitored for
13 each combustion test. Each combustion test is
14 approximately 5 to 15 minutes in duration. Therefore,
15 based on the recording frequency noted for each parameter
16 in Table C-3, each parameter will be recorded at least once
17 every 15 minutes.

18

19 **Table C-3. Combustion Test Monitoring**

Parameter	Minimum Recording Frequency
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

20

21 Temperature-Inlet 1 will be recorded at the end of the
22 temperature ramp-up for gasification to monitor the
23 pyroprobe final temperature.

24

25

26 The flow rate of the exhaust gas routed to the bubblers
27 (described in Section 5.2) will be determined based on the
28 flow measurements listed in Table C-3.

29

30 The amount of material fed to the system will be verified
31 by weighing the pyroprobe insert cartridge before and after
32 each experiment.

33

34 Exhaust gas oxygen concentration will be calculated, based
35 on measured total input flow rate of synthetic air and fuel
36 assuming complete combustion.

1
2 5. Sampling and Analysis

3
4 5.1 Exhaust Gas Monitoring

5
6 Combustion exhaust gas will be monitored for carbon
7 monoxide (CO) and CO₂ via the in-line GC using a molecular
8 sieve column and MSD or via off-line analysis of exhaust
9 gas collected in Tedlar® bags.

10
11 5.2 Exhaust Gas Sampling

12
13 Gas samples for off-line analysis will be collected from a
14 vent line off the interface. Flexible (silicone or
15 equivalent) tubing will connect the vent line and a set of
16 bubblers.

17
18 Gas absorption via these bubblers will provide aqueous
19 solution (of documented content) to analyze for the
20 parameters in Section 5.3. Two to four bubblers (low
21 pressure drop impingers) in series will be used. Each
22 bubbler will contain a predetermined amount of aqueous
23 solution. The temperature of the gas exiting the last
24 bubbler will be monitored.

25
26 An additional empty bubbler will be added to the front end
27 of this series of bubblers to serve as a knock-out pot if
28 stoichiometric calculations (see Sections 2 and 4.3) for
29 the test substance or experience from earlier combustion
30 testing with test substance indicate that greater than 10
31 mL of water will be produced during the combustion test of
32 a given test substance.

33
34 Upon completion of sample collection, the amounts in each
35 bubbler will be determined by observation or by weight, and
36 the contents of the bubblers will be composited for
37 subsequent analysis. Additionally, the flexible tubing
38 will be rinsed with 5 mL of HPLC water to collect potential
39 condensate in the tubing; this rinsate will be combined
40 with the bubbler composite prior to analysis.

41
42 A minimum of 60 mL of bubbler aqueous solution is expected
43 from each combustion test. Of this, a minimum of 45 mL
44 will be sent for PFOA analysis, a minimum of 5 mL will be
45 sent for fluoride (and chloride) ion analysis, and a
46 minimum of 2 mL will be sent for total fluorine analysis.

1 Bubbler aqueous solutions will be conveyed to analytical
2 laboratories in a polyethylene, polypropylene, or glass
3 containers.

4 5 5.3 Exhaust Gas Analysis

6 7 5.3.1 Fluoride & Chloride Ion

8
9 A portion of the composite aqueous solution sample from
10 each combustion test collected as described in Section 5.2
11 will be analyzed for fluoride ion and for chloride ion via
12 ion chromatography.

13 14 5.3.2 Total Fluorine

15
16 A portion of the composite aqueous solution sample from
17 each combustion test collected as described in Section 5.2
18 will be analyzed for total fluorine via Wickbold Torch at a
19 qualified laboratory; see Attachment C-1.

20 21 5.3.3 PFOA

22
23 A portion of the composite aqueous solution sample from
24 each combustion test collected as described in Section 5.2
25 will be analyzed for PFOA via LC/MS/MS at a qualified
26 commercial laboratory in accordance with "Method of
27 Analysis for the Determination of Ammonium
28 Perfluorooctanoate (APFO) in Water Revision 1" (EPA Docket
29 ID OPPT-2003-0012-0040) as revised for exhaust gas bubbler
30 sample analysis for PFOA. See Attachment C-5 for these
31 revisions and for the limit of quantitation (LOQ) for each
32 relevant matrix in this test program.

33
34 Due to background levels of PFOA, the analytical laboratory
35 will only report numerical values for PFOA concentration in
36 the aqueous solution greater than or equal to the LOQ.
37 This is required to assure that the reported concentration
38 value is attributable to the sample rather than to
39 background.

40 41 5.4 Test Substance Sampling & Analysis

42
43 See Section 1.
44
45
46

1 6. Reporting of Results

2
3 6.1 Elemental Analysis Results

4
5 The results of elemental analysis of the test substance
6 composites (as noted in Section 1) will be reported. The
7 laboratory reports will be included in an appendix to the
8 test report.

9
10 6.2 Combustion Stoichiometry Results

11
12 Combustion stoichiometry (as noted in Section 2)
13 calculations will be included in an appendix to the test
14 report.

15
16 6.3 TGA Results

17
18 TGA graphical results for test substance composites (as
19 noted in Section 3) will be included in an appendix to the
20 test report.

21
22 6.4 Combustion Test Results

23
24 6.4.1 Process Monitoring

25
26 Process monitoring data (as noted in Section 4.5) recorded
27 for each combustion test will be reported in tabular form.

28
29 6.4.2 Exhaust Gas Monitoring

30
31 Exhaust gas CO and CO₂ monitoring results will be reported
32 as the integrated value for each combustion test. CO will
33 be reported in terms of parts per million by volume (ppmv).
34 CO₂ will be reported in terms of percent by volume (%).

35
36 6.4.3 Exhaust Gas Results

37
38 Results of analyses noted in Section 5.3 will be reported
39 for each combustion test.

40
41 The analytical result for each analyte in Section 5.3 will
42 be reported in terms of concentration (mass per volume) in
43 the aqueous solution. For each analyte, this value will be
44 used with the associated exhaust gas volume to compute an
45 exhaust gas concentration.

1 6.4.3.1 Fluoride and Chloride

2
3 Fluoride ion and chloride ion in the exhaust gas will be
4 reported in terms of concentration (mass of ion per volume
5 of exhaust gas) in the gas and on the basis of mass of ion
6 per mass of test substance. The corresponding hydrogen
7 halide value for each will also be computed and reported
8 for reference.

9
10 The fluorine ion value is also the total inorganic fluorine
11 value.

12
13 6.4.3.2 Total Fluorine and Total Organic Fluorine

14
15 Total fluorine in the exhaust gas will each be reported in
16 terms of concentration (mass of fluorine per volume of
17 exhaust gas) in the gas and on the basis of mass of
18 fluorine per mass of test substance.

19
20 Total organic fluorine will be determined by difference
21 between total fluorine and total inorganic fluorine.

22
23 6.4.3.3 PFOA

24
25 PFOA in the exhaust gas will be reported in terms of
26 concentration in the gas (mass of PFOA per volume of
27 exhaust gas). If present at a concentration above the
28 matrix-specific LOQ, PFOA in the exhaust gas will also be
29 reported on the basis of mass of PFOA per mass of test
30 substance.

31
32 6.5 Test Substance Results

33
34 Elemental compositions will be reported as indicated in
35 Section 6.1 above.

36
37 6.6 Release Assessment

38
39 In the event that PFOA is found in the exhaust gas at a
40 concentration above the LOQ for the average of three runs
41 for a given test substance composite, then the potential
42 for release from full-scale waste incineration of the
43 subject material will be assessed to inform the basis for
44 possible next steps.

45
46 This assessment will consider a number of factors such as
47

- 1 • PFOA results from this testing program reported per
2 Section 6.4.3.3,
3 • estimated amounts of subject material in feed to full-
4 scale waste incinerators, and
5 • degree of post-combustion air pollution control (e.g.,
6 use and effectiveness of carbon adsorption).
7
8

9 *[Section 6.6 as presented is based on the September 12,*
10 *2003 Detailed Test Protocol Outline (as discussed at the*
11 *August and September ECA Technical Work Group meetings) and*
12 *will be elaborated on by the Drafting Committee]*
13
14
15

16 Attachments

17 *[numbered according to the relevant Appendix and*
18 *Section number]*
19

20 Attachment C-1 Wickbold Torch
21 *[under development]*
22

23 Attachment C-3 TGA: Annotated ASTM E1868
24 *[under development]*
25

26 Attachment C-4 Waste Incineration and Operating Conditions
27 *[same as the Appendix from the 9-12-03 Detailed Test*
28 *Protocol (with minor revision)]*
29

30 Attachment C-5 PFOA Analysis
31 *[under development]*