

Fluoropolymer Technical Work Group

Incineration Test Protocol
Outline

September 17, 2003

Discussion Objective

- Review test protocol outline for understanding
- Determine next steps

Outline

1. Introduction
 2. Test Objective
 3. Experimental Approach
 4. Materials and Methods
 5. Combustion Test Sampling and Analysis
 6. Reporting of Results
- Appendix

Introduction

- Overall objective of test program is to determine if incineration of fluoropolymers is a potential source of PFOA to the environment
- Submission was an outline as agreed; additional detail to be developed pending agreement on outline
- QAPP addressing QA/QC to be developed as well

Research Program

- Much work needed to integrate sampling & analytical methods for PFOA into an incineration experimental program
- Initial focus will be on demonstrating proposed methods are capable of meeting data quality objectives (DQOs)
- Need provision to obtain approval to modify test program if do not appear able to provide information meeting DQOs

Test Objective

- Investigate incineration of fluoropolymers under laboratory-scale conditions representative of typical municipal waste combustor operations in the U.S. to quantitatively determine potential emission levels of PFOA

Experimental Approach

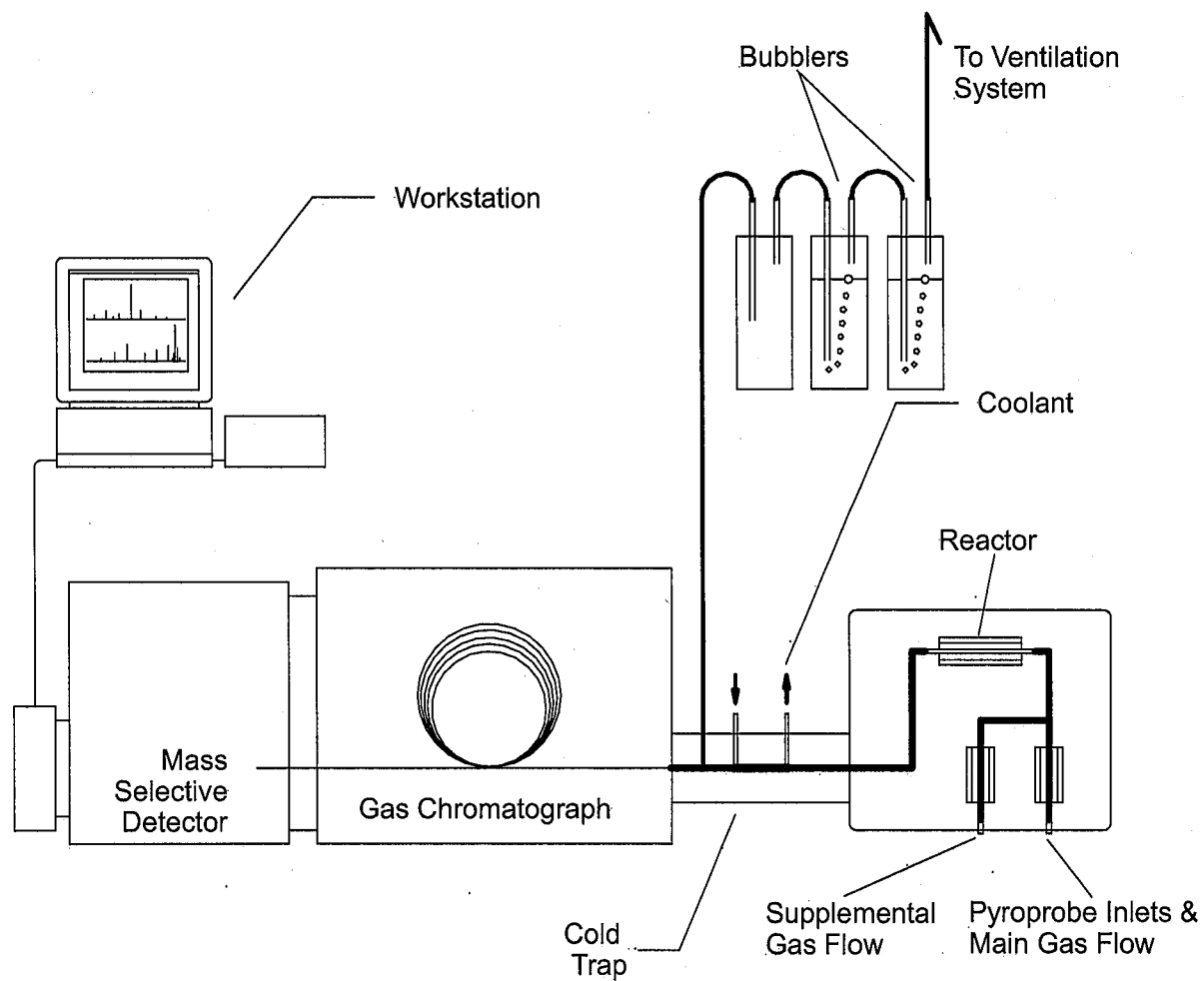
- Conduct elemental analysis of test feeds to define stoichiometry
- Perform TGA to inform conditions for test material gasification in combustion tests
- Verify quantitative transport of PFOA
- Conduct combustion tests

Combustion Test Materials & Methods

Test Feed	Dry melt resin composite	PTFE composite	Fluoro-elastomer composite	Aqueous dispersion composite
Temperature	900 °C	900 °C	900 °C	900 °C
Residence Time	2 sec	2 sec	2 sec	2 sec
Excess O₂	10 %	10 %	10 %	10 %
No. of runs	3	3	3	3
No. of thermal blanks	≥1	≥1	≥1	≥1

Note: planned temperature reflects low end of typical MWC operations

Advanced Thermal Reactor System



9/17/03

presentation to
Fluoropolymer Technical Work Group

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Combustion Test Sampling & Analysis

- Exhaust Gas
 - Monitored parameters (CO, CO₂, O₂, flow)
 - Sampling
 - Aqueous solution bubblers planned
 - Analysis
 - Fluoride ion (total inorganic fluorine) via ion-selective electrode or ion chromatography
 - Total fluorine via Wickbold torch
 - Total organic fluorine by difference (between Total fluorine and Total inorganic fluorine)
 - PFOA via LC/MS/MS

Combustion Test Sampling & Analysis

- Test Material Composites
 - Elemental analysis (C, H, N, F, S, O)
 - Note: for these materials, total organic fluorine is equivalent to total fluorine

Reporting of Results

- Exhaust Gas Results
- Test Material Results
- Exposure Assessment

Discuss Next Steps

9/17/03

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Detailed Test Protocol Outline

Proposal, September 12, 2003

1. Introduction

The overall goal of this program is to determine if incineration of fluoropolymers (in applications where incineration is a commonly used disposal practice) is a potential source of PFOA to the environment.

This document presents a detailed outline of a protocol for a research program to conduct incineration testing. Substantial preparatory work is necessary to integrate available sampling and analytical methods for PFOA into an experimental program for incineration testing.

Following agreement on this document, a test protocol and Quality Assurance Project Plan (QAPP) can be prepared. The QAPP will include data quality objectives (DQOs). Although alternative methods are included herein to the extent practicable, it is anticipated that the administration of this program will allow for obtaining approval to modify the test program (e.g., to substitute alternate test methods) in case(s) where proposed method(s) do not appear able to provide information meeting these DQOs.

The QAPP will also address other quality assurance/quality control elements for this test program, including project organization, chain of custody, and sample container selection.

Details of this test protocol are outlined in subsequent sections. The test objective is presented in Section 2. Section 3 discusses the overall experimental approach and preliminary testing prior to the combustion tests. Section 4 presents the materials and methods involved in this test program with focus on combustion testing. Plans for sampling and analysis are described in Section 5. Section 6 reviews how results of this program will be reported.

2. Test Objective

The specific objective of this test program is to investigate incineration of designated fluoropolymers under laboratory-scale conditions representative of typical

municipal waste combustor operations in the U.S. to quantitatively determine emission levels of PFOA.

3. Experimental Approach

Each test material (as described in Section 4.2) will undergo elemental analysis (see Section 5.2) to define the basic parameters for stoichiometric calculations.

Thermogravimetric analysis (TGA) per ASTM E1641 will be conducted to determine the gasification temperature of each test material. TGA will be performed on each sample to determine the temperature range required for gasification of the sample and ash content. This analysis will be conducted in flowing air from room temperature to 1000°C at 25°C/minute using 3 to 5 mg samples. The temperature for 100% gasification for each test material will be considered in establishing conditions for the gasification section (pyroprobe section) of the experimental apparatus for the combustion tests; see section 4.3.

Overall, stoichiometry and TGA results will form the basis for setting experimental conditions (e.g., time and temperature) in the gasification section of the experimental system during the combustion tests.

Combustion tests will be carried out at specified operating conditions as presented in Section 4.3.

Prior to combustion testing, quantitative transport of PFOA will be verified. For these transport tests, plans call for gasifying nominally 1 mg of PFOA at 150 to 200 °C with transfer line and reactor temperatures nominally 30 to 50 °C higher than the gasification temperature. The exhaust gas will be sampled and analyzed as described in Section 5.1.4 to determine quantitation of PFOA. If the PFOA transport efficiency is found to be less than a specified level (e.g., 70%), then the reactor would be disassembled and extracted with an appropriate solvent (e.g., methanol). This solvent sample would be analyzed via the analytical method described in Section 5.1.4 to determine if adsorption on the reactor walls is responsible for the low recovery. The experimental apparatus described in Section 4.1 is configured such that additional extractions of the transfer lines between the pyroprobe and the reactor and

between the reactor and the downstream sampling point are not feasible.

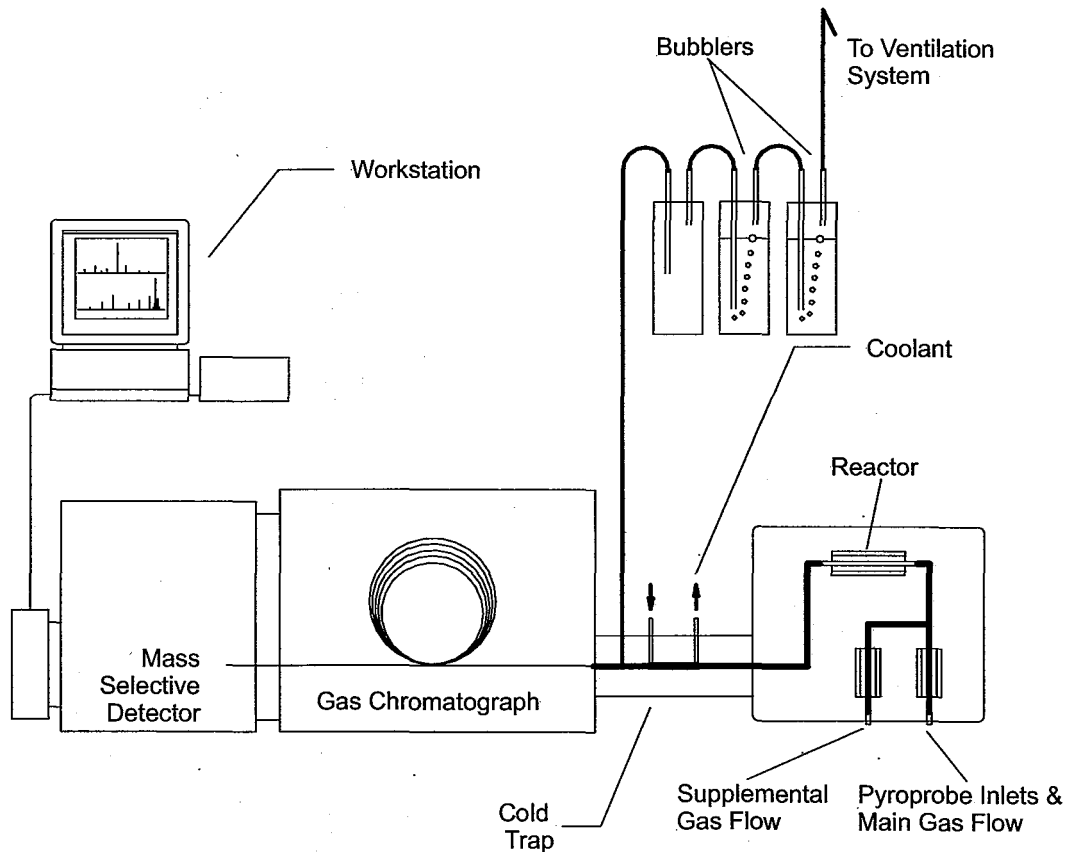
4. Materials and Methods

4.1 Combustion Test Experimental Apparatus

Incineration testing is to be accomplished using a batch-charged continuous flow reactor system. The test sample is gasified and transported to a high temperature reactor. In the high temperature reactor, the sample vapors are subjected to controlled conditions of residence time, temperature, and excess air. Combustion products are collected for quantitative analysis.

Use of the Advanced Thermal Reactor System (ATRS) at the University of Dayton Research Institute (UDRI) is planned. A schematic of the ATRS as planned for use in this test program is presented in Figure 1.

Figure 1. Schematic of ATRS for Planned Testing



Supplemental gas flow and main gas flow refer to the planned gas feeds (synthetic air and methane).

The ATRS consists of a reactor assembly and in-line gas chromatograph/detector system connected via a cryogenic interface. The reactor assembly consists of a thermally insulated enclosure housing the sample introduction, reactor, and transfer line systems. Sample introduction for solid materials employs a pyroprobe, a device designed to gasify samples by heating them at a fixed rate. During combustion tests, the transfer line between the pyroprobe and the reactor is heated and maintained above 250 °C. The reactor is housed within its own small tube furnace and may be independently heated to as high as 1200 °C. (Actual conditions planned for this test program are presented in Section 4.3.) The exhaust line from the reactor is heat traced to prevent cool regions where reactor products could otherwise be lost through condensation. The cryogenic interface (cold trap) is of a shell and tube design and provides significant cooling of the combustion exhaust gas prior to on-line monitoring or sample collection.

For this test program, plans call for setting the cold trap temperature at nominally -15 °C to be below the freezing point of water (H₂O) but above the sublimation temperature of carbon dioxide (CO₂) to assist in separating H₂O from carbon monoxide (CO) and CO₂.

The in-line gas chromatograph (with molecular sieve column) and mass selective detector (MSD) are planned to be used to monitor CO and CO₂. Exhaust gas samples for off-line analysis will be collected from the vent line off the cold trap; see Section 5.1.

4.2 Test Materials

Four test materials are planned for this study. Each will be a composite mixture of representative fluoropolymers, as solids, in equal proportions across producers for each of the following four classes:

- Dry melt resins (FEP, PFA, THV, ETFE, HTE)
- PTFE
- Fluoroelastomers
- Aqueous dispersions (PTFE, FEP, PFA, THV)

4.3 Combustion Test Experimental Conditions

The test materials described in Section 4.2 will be subjected to laboratory-scale incineration using the experimental apparatus described in Section 4.1.

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

Methane will be used as needed as a supplemental fuel to ensure the presence of sufficient hydrogen to convert fluorine to hydrogen fluoride (HF).

The planned operating conditions for the high temperature reactor during the combustion tests are 900 °C with 2 seconds gas residence time and 10% oxygen in the exhaust gas. As the Appendix indicates, these conditions are representative of typical operating conditions for the high temperature zone of municipal waste combustors (MWCs) in the U.S., except that the planned temperature reflects the low end of normal MWC operating temperatures. Also, as the information in the Appendix indicates, the planned temperature is less than typical secondary chamber operating temperatures for medical waste incinerators in the U.S.

As noted in Table 1, three replicates are planned for each test level (combination of test material and temperature).

Table 1

Test Material	Dry melt resin composite	PTFE composite	Fluoroelastomer composite	Aqueous dispersion composite
Temperature	900 °C	900 °C	900 °C	900 °C
No. of runs	3	3	3	3

Additionally, at least one thermal blank (with combustion test feeds except for the test material) is planned for each group of 3 runs.

The amount of test material fed will be large enough to assure ability to detect PFOA in the emissions, but small enough to assure sufficient excess oxygen to be representative of typical MWC conditions. While elemental analysis and TGA is required to establish the planned mass

of sample, the expected sample size is on the order of 1 to 2 mg.

The temperature in the pyroprobe section will be maintained at approximately 50 to 100 °C above the highest temperature for 100% gasification across the test materials as determined from the thermogravimetric experiments earlier in the test program. This is necessary to assure complete gasification of the sample of test material and a common set of experimental conditions across the test materials during combustion testing.

5. Combustion Test Sampling and Analysis

5.1 Exhaust Gas Sampling & Analysis

Gas samples for off-line analysis will be collected from a vent line off the cold trap and may be subjected to additional external cooling (e.g., ice bath) as needed.

Analysis of the exhaust gas samples of the thermal blanks will focus on PFOA since the primary purpose of conducting these blank runs is to check for possible cross-contamination between sample runs.

5.1.1 Monitored Parameters

As noted in Section 4.1, on-line monitoring for CO and CO₂ via the in-line GC using a molecular sieve column and MSD is planned. Alternately, Tedlar® bag samples of exhaust gas may be collected for off-line CO and CO₂ analysis.

Exhaust gas flow rate will be monitored based on measured input flow rates of the synthetic air and methane gas feeds. Exhaust gas oxygen concentration will be calculated, based on measured input flow rate of synthetic air and methane assuming complete combustion.

5.1.2. Fluoride

The exhaust gas will be sampled and analyzed for fluoride ion to assist in performing a fluoride balance across the experimental system.

Fluoride ion will be sampled via absorption into aqueous solution, using bubblers (low pressure drop midget

impingers) in series. As Figure 1 indicates, initial plans call for using three bubblers in series with the first one empty to serve as a knock-out pot and the second and third containing a predetermined amount of aqueous solution. (The number of aqueous solution bubblers will be adjusted as necessary.) Upon completion of sample collection, the amounts in each bubbler will be measured and the contents of the bubblers will be quantitatively transferred into a container for subsequent analysis for total inorganic fluorine (i.e., fluoride ion) via ion chromatography or ion selective electrode.

5.1.3 Total Fluorine

The aqueous solution sample collected as described in Section 5.1.2 is also planned to be subjected to analysis for total fluorine via Wickbold torch so that total organic fluorine can be determined by difference between total fluorine and total inorganic fluorine. Work is in progress to confirm that detection limits for total fluorine analysis via Wickbold torch are low enough to be informative for this test system.

5.1.4 PFOA

Exhaust gas samples will be analyzed for PFOA via LC/MS/MS at a qualified commercial laboratory operating under suitable data quality guidelines.

Development is in progress to define the most suitable sampling technique for PFOA in the incineration exhaust gas.

Initial plans call for using the aqueous solution bubblers described in Section 5.1.2 to collect PFOA from the exhaust gas and for sending a portion of the aqueous solution for PFOA analysis as described above. Additionally, an attempt will be made to use an OSHA Versatile Sampler (OVS) as a back-up sampling device. If OVS is also used to sample PFOA in the exhaust gas, then the OVS would also be sent for off-line LC/MS/MS analysis to quantify PFOA as a cross-check on the aqueous solution bubbler results.

5.2 Test Material Sampling & Analysis

Each test material composite will undergo elemental analysis for carbon, hydrogen, nitrogen, fluorine, sulfur,

and oxygen by difference. Ultimate analysis (ASTM D3176 and other ASTM methods referenced therein) are planned for this analysis. Moisture is also determined by this method. Depending on sample size, it may be necessary to implement the microanalytic analog of ultimate analysis.

Based on process knowledge, the level of total fluorine in the test materials is orders of magnitude higher than the potential level of inorganic fluoride in these materials. Therefore, for this test program, plans call for assuming that the total organic fluorine value for each test material composite is the same as the fluorine value determined via elemental analysis as described above.

6. Reporting of Results

6.1 Exhaust Gas Results

6.1.1 Monitored Parameters

CO will be reported in terms of parts per million by volume (ppmv). CO₂ will be reported in terms of percent by volume (%). Oxygen will be reported in terms of percent by volume (%). Exhaust gas flowrate will be reported in units of cubic centimeters per minute (cm³/min).

6.1.2 Fluoride and Fluorine

Total fluorine and fluoride (total inorganic fluorine) in the exhaust gas will each be reported in terms of concentration (mass of fluorine per volume of exhaust gas) in the gas as well as on the basis of mass of fluorine per mass of starting test material.

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

6.1.3 PFOA

PFOA in the exhaust gas will be reported in terms of concentration in the gas as well as on the basis of mass per mass of starting test material.

6.2 Test Material Results

Elemental compositions will be reported in terms of mass per mass of composite feed material.

6.3 Exposure Assessment

In the event that PFOA is found in the exhaust gas at a concentration above the limit of quantitation (for the matrix) from one or more experiments described in this protocol, then the potential for exposure related to incineration of the subject material will be assessed to inform the basis for possible next steps.

This assessment will consider a number of factors such as

- Test program-determined PFOA emission factor,
- estimated amounts of subject material in feed to full-scale waste incinerators, and
- degree of post-combustion air pollution control (e.g., use and effectiveness of carbon adsorption).

Appendix

Polymers of the sort being investigated in this test program may be present at trace to low concentrations in municipal solid waste or in medical waste and therefore may be incinerated.

A.1 Types of Incinerators

A.1.1 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 A-1 summarizes the number and annual capacity of these units by type of technology employed.

Table A-1. MWCs in 2002

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

As the capacity values indicate, modular units are generally small MWCs accounting for less than a total of 2% of the municipal solid waste incinerated in the U.S. in 2002.

A.1.2 Hospital/Medical/Infectious Waste Incinerators

Although earlier reports indicated over 2200 medical waste incinerators in the U.S. in the 1990s (EPA 2000a), 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.

A.2 Operating Conditions

As noted by EPA, 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)

Speaking of 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 are expected to typically operate with a 2 second gas residence time in the high temperature zone in order to assure compliance with emission standards on carbon monoxide and dioxins.

A.2.1 MWC Operating Conditions

EPA presents operating data for some MWCs in "Municipal Waste Combustion Assessment: Technical Basis for Good Combustion Practice" and points the reader elsewhere for additional data on specific representative MWCs.

Modular MWC

Specifically, this background document (EPA 1989) includes secondary chamber temperatures for modular MWCs that had CO emission levels less than current emission standards, and these are summarized in Table A-2.

Table A-2. Modular MWC Temperatures

Secondary Chamber Temperature (°C)	Oswego Co., NY	Red Wing, MN
Start of campaign	1012	
Mid-range secondary temperature	951	
End of campaign	995	
Low secondary temperature	885	
Mean secondary temperature		954 - 1071

As highlighted in Table A-2, typical secondary chamber temperatures for these dual-chamber modular units are in the range of 951 to 1071 °C.

As indicated in section A.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.

Although this 1989 EPA background document does not present temperature data for mass burn nor RDF units, reports from the National Incinerator Testing and Evaluation Program (NITEP) present operating data for an RDF combustor (Mid-Connecticut) and for a mass burn waterwall combustor (Quebec City) otherwise discussed in the 1989 background document.

RDF MWC

Furnace temperatures and flue gas oxygen 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 A-3.

Table A-3. 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

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

Mass Burn MWC

Furnace temperatures (average of front and rear radiation chamber temperatures) and flue gas oxygen levels (dry basis) for Quebec City mass burn combustor performance tests operating under good combustion conditions across a

range of steam loads (Environment Canada 1988) are summarized in Table A-4.

Table A-4. Mass Burn MWC - Quebec City

Steam load	Low	low	Low	design	design	Design	High	high
test number	PT02	PT10	PT11	PT05	PT06	PT12	PT07	PT09
Furnace temperature (°C)	849	875	869	1014	1030	992	1085	1006
flue gas O ₂ (dry)	13	13	12	9	9	10	10	10

The average operating conditions for this mass burn unit across the range of steam loads are 965 °C and 10.8% O₂. When operated at design steam load, the average operating conditions for this mass burn MWC are 1012 °C and 9.3% O₂.

MWC Summary

Considering the relative quantities of municipal waste burned annually in each type of MWC and the data in this section, average typical operating conditions for the high temperature zone of MWCs are nominally 1000 °C and 10% O₂.

A.2.2 HMIWI Operating Conditions

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.

Theodore reports the range of temperatures for the secondary chamber of controlled air medical waste incinerators 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)

As noted above, a more recent report indicates that existing HMIWIs operate with secondary chamber temperatures greater than or equal to 1000 °C with a gas residence of 2 seconds. (Van Remmen 1998)

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