EPA/600/A-94/008

ORGANIC EMISSIONS FROM PILOT-SCALE INCINERATION OF CFCS

Jeffrey V. Ryan
Acurex Environmental Corporation
4915 Prospectus Drive
P.O. Box 13109
Research Triangle Park, NC 27709

C. W. Lee
U.S. Environmental Protection Agency
Air and Energy Engineering Research Laboratory
Research Triangle Park, NC 27711

Steven Korn
T-Thermal Inc.
Brook Road
Conshohocken, PA 19028

ABSTRACT

As a result of the Montreal Protocol, an international accord implemented to reduce the production and use of stratospheric ozone depleting substances, considerable quantities of chlorofluorocarbons (CFCs) and halons may be accumulated and may ultimately require disposal or destruction. Incineration is a potential destruction technology; however, little is known of the combustion emission characteristics from incinerated CFCs. A study has been performed that characterizes the organic emissions resulting from the pilot-scale incineration of trichlorofluoromethane (CFC-11) and dichlorodifluoromethane (CFC-12) under varied feed concentrations. A 290 kW (1,000,000 Btu/h) incinerator was made available to the U.S. Environmental Protection Agency (EPA) for these tests. The emissions characterizations focused on determining the destruction and removal efficiencies (DREs) and major products of incomplete combustion (PICs) for each CFC evaluated. Sampling was performed to screen for volatile and semivolatile organic emission products including chlorinated aliphatics, chlorobenzenes, chlorophenols, polychlorinated dibenzodioxins and furans (PCDDs and PCDFs), and polyaromatic hydrocarbons (PAHs). Results indicate that five nines (99.999 percent) DRE can be achieved at a CFC-11 feed concentration as high as 69 percent by mass. The formation of volatile and semivolatile organic PICs was minimal. "Less than" concentrations are presented for target analytes not detected. Total PCDD/PCDF emission concentrations did not exceed 140 ng/m^3. The injection of water into the combustion zone may improve the thermal destruction process.

INTRODUCTION

Halogenated hydrocarbons, such as chlorofluorocarbons (CFCs) and halons, have been implicated in the depletion of stratospheric ozone. International accords are in place to phase out the production and/or use of these ozone-depleting substances (ODSs) by the end of the century. Although some of these CFCs will be recycled, it may be necessary to destroy substantial quantities of some CFCs to reduce current inventories. A United Nations Environment Programme (UNEP) technical advisory committee was formed in 1991 to evaluate the most appropriate ODS destruction technologies. Incineration was identified as a potentially viable CFC destruction technology. However, the combustion emissions from CFC incineration have not been well characterized. Characterization of products of incomplete combustion (PICs), in addition to determination of destruction and removal efficiencies (DREs), is required to fully evaluate the viability of incineration as a CFC destruction technology.

Relatively little information is available regarding CFC incineration, particularly in the area of PIC characterization. Dickerman et al. collected data indicating that various CFCs have been destroyed effectively by full-scale incineration.[1] No data on PIC formation were included. The Air and Energy Engineering Research Laboratory (AEERL) of the U.S. Environmental Protection Agency (EPA) initiated a program to evaluate the viability of CFC incineration, including characterization of PICs. In support of this program, a bench-scale study that characterized the emissions from CFC-11 (trichlorofluoromethane) and CFC-12 (dichlorodifluoromethane) incineration was performed.[2] An emission sample was collected during the 8.3 percent (by volume) CFC-12

feed concentration test to screen for polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polyaromatic hydrocarbons (PAHs). The PCDD/PCDF screening revealed that relatively high concentrations of PCDD/PCDF (23.8 $\mu g/m^3$ total PCDD/PCDF) were present in the incineration emissions. These results were somewhat surprising, as the probability of gas-phase PCDD/PCDF formation is likely to be very low at high temperatures.[3] Heterogeneous PCDD/PCDF formation was considered unlikely because both fuel and CFC were introduced as gases and no particulate was observed during this test.[2] More representative CFC incineration emissions data were needed to substantiate or refute this finding.

The primary objectives of this AEERL-sponsored study were to characterize organic emissions resulting from the incineration of CFCs under operating conditions typical of commercial incineration facilities as well as confirm or refute the presence of PCDD/PCDF emissions at concentrations similar to those observed during the previous AEERL-sponsored CFC incineration study.[2] Particular emphasis was placed on PIC characterization. Should similar high PCDD/PCDF emission concentrations be observed, the screening of incinerator emissions for volatile and semivolatile organic PICs may provide insight into potential PCDD/PCDF formation precursors or intermediates.

Through an agreement with the EPA, T-Thermal Inc. made available one of their Conshohocken, PA, pilot-scale test facilities to evaluate the incineration of CFC-11 and CFC-12. Under this agreement, T-Thermal Inc. provided the equipment and labor resources necessary to prepare and operate the facility for the CFC incineration tests. Acurex Environmental directed these tests, including coordination of sampling and analytical efforts.

EXPERIMENTAL

The incineration tests were performed at T-Thermal Inc.'s Conshohocken, PA, test facility. The test materials (CFC-11 and CFC-12) were incinerated at several feed concentrations. A total of four tests were performed. Table I presents the target CFC feed concentrations for each test. A combustion blank (no CFC incineration) was included as a test condition.

TABLE I. TARGET CFC FEED CONCENTRATIONS

Test	Condition
1	No. 2 fuel only
2	3 % (by mass) CFC-12/balance No. 2 fuel oil
3	3 % (by mass) CFC-11/balance No. 2 fuel oil
4	50 % (by mass) CFC-11/balance No. 2 fuel oil

Emissions samples were collected for volatile and semivolatile organics and subsequently analyzed to determine DREs and screen for PICs. Emissions were sampled downstream of all pollution control devices. Scrubber water samples were also collected to screen for semivolatile organic PICs. Because of limited access to the test facility, each test was limited to approximately 2 hours in duration. This allowed two test conditions to be evaluated daily.

The T-Thermal pilot-scale test facility is a down-fired, turbulent-flame incinerator nominally rated at 290 kW (1 MMBtu/h). A diagram of the test facility is presented in Figure 1. The incinerator consists of a T-Thermal LV-1.3 high intensity vortex burner mounted tangentially near the top of the vertical, refractory-lined incineration chamber. The No. 2 fuel oil and the CFC waste stream were introduced through the side-mounted burner, while cooling water was introduced through the axially mounted top injector. The cooling water was injected into the flame region to maintain a consistent incineration temperature of 1,093 °C (2,000 °F).

A thermal externally atomized tip (TEAT) injector was used to atomize the fuel oil/CFC waste stream. The injector consists of three concentric pipes: the outer pipe providing atomizing air, an inner tube supplying fuel oil, and the innermost pipe feeding the CFC waste stream. The fuel oil and CFC waste were mixed at the injector tip. Combustion air was introduced to the system through the LV-1.3 windbox. In the incineration chamber, the atomized fuel and waste stream combined with the combustion air through the induced vortex action to sustain combustion and destroy the waste stream. The nominal residence time was 1.5 seconds.

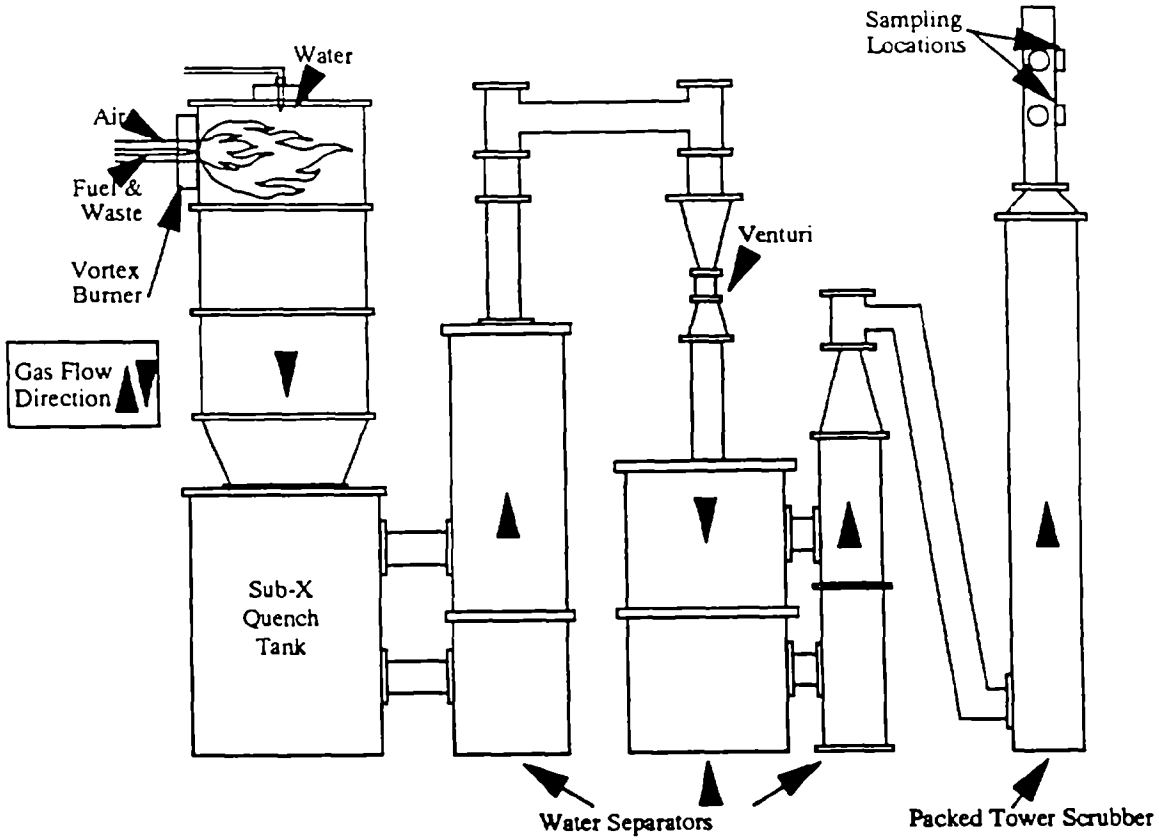

Figure 1. T-Thermal incineration facility.

Hot gases leaving the incinerator passed through a quench tank which contains a water-washed downcomer and a pH-controlled water bath. The quench tank also served to transfer the heat from the hot gases exiting the incineration chamber to the water bath. An alkaline solution (potassium hydroxide) was added to the quench tank to neutralize acid gases. The water-saturated gases exited the quench tank at approximately 88 °C (190 °F) and entered a venturi scrubber for particulate and further acid gas removal. A pH-controlled packed-tower scrubber neutralized any remaining acid gases.

Volatile and semivolatile organic incineration emissions were collected using conventional sampling methodologies. Volatile organics were collected in Tedlar® bags as described in EPA Method 18.[4] Semivolatile organics, including PCDDs and PCDFs, were collected using EPA Method 23.[5] All samples were collected downstream of the pollution control equipment. Duplicate samples were collected simultaneously for each test condition. Scrubber liquor samples from each of the three system reservoirs were collected to screen for semivolatile organic PICs as well.

Volatile organics, including CFCs, were analyzed by gas chromatography/mass spectrometry (GC/MS).[4,6] The Method 23 samples were analyzed for semivolatile organics, including PCDDs and PCDFs, by high resolution gas chromatography (HRGC) coupled with low resolution mass spectrometry (LRMS).[7,8] The analytical procedure used differs from the stated method in that individual PCDD/PCDF isomers were not identified. The sampling train components (filter, XAD-2, and rinses) were extracted and analyzed as a single sample. All Method 23 samples were analyzed for PCDDs and PCDFs. Only half of the Method 23 samples were screened for other semivolatile organic PICs. The analytes targeted were limited to those considered to be potential PCDD/PCDF precursors. These target analytes included chlorobenzenes (CBs), chlorophenols (CPs), and PAHs. Instrument detection levels were also determined for these analytes.[9]

The scrubber water samples were extracted as described in EPA Method 8280.[7] Separate samples were extracted for PCDD/PCDF and semivolatile organic PIC analyses.

RESULTS AND DISCUSSION

Incinerator operational data are summarized in Table II. The data presented are based on the average measurements taken over each test period. The CFC feed concentrations are presented as a percentage of the sum of fuel and waste mass flows. The CFC feed concentrations obtained were in accordance with those established in the original test matrix. However, the high CFC feed concentration was significantly greater than the targeted level (68.9 percent as opposed to 50 percent). The 50 percent feed concentration was targeted to represent the maximum feed concentration likely to be employed. Of the data available pertaining to full-scale incineration facilities, the greatest CFC feed concentration identified was 23.6 percent.[1]

TABLE II. T-THERMAL INCINERATOR OPERATIONAL DATA

	Test 1	Test 2	Test 3	Test 4
Primary Combustion Air Flow - kg/h (lb/h)	285.7 (629.3)	293.7 (647.0)	300.5 (661.8)	295.3 (650.5)
Secondary Combustion Air Flow - kg/h (lb/h)	100.9 (222.3)	106.4 (234.3)	106.9 (235.5)	110.8 (244.0)
Purge Air Flow - kg/h (lb/h)	8.6 (19.0)	9.2 (20.3)	9.8 (21.5)	9.1 (20.0)
Cooling Water Flow - kg/h (lb/h)	NA	14.7 (32.4)	9.1 (20.1)	8.7 (19.2)
No. 2 Fuel Oil Flow - kg/h (lb/h)	16.2 (35.6)	19.1 (42.0)	18.5 (40.8)	18.8 (41.4)
CFC-12 Flow - kg/h (lb/h)	0.0	0.5 (1.0)	0.0	0.0
CFC-11 Flow - kg/h (lb/h)	0.0	0.0	0.5 (1.2)	41.6 (91.7)
Total Fuel/CFC Flow - kg/h (lb/h)	16.2 (35.6)	19.5 (43.0)	19.1 (42.0)	60.4 (133.1)
% CFC of Total Flow	0.0	2.3	2.9	68.9
% Excess Air	25.1	6.2	12.0	-6.1
Firing Rate - kW (MMBtu/h)	198 (0.676)	234 (0.797)	227 (0.776)	246 (0.839)
Incinerator Temperature - °C (°F)	1,070 (1,958)	1,092 (1,998)	1,092 (1,998)	1,121 (2,049)
Oxygen (% dry)	15.9	8.9	9.0	7.3
Carbon Dioxide (% dry)	7.0	10.7	9.3	10.6
Carbon Monoxide (ppmv dry)	0	8	10	15
Nitrogen Oxides (ppmv dry)	65	43	149	50

NA = Not available

Five nines (99.999 percent) DRE was achieved for the CFC-12 low feed concentration (2.3 percent) and the CFC-11 high feed concentration (68.9 percent) tests. Only three nines (99.9 percent) DRE was achieved for the CFC-11 low feed concentration (2.9 percent) test. A reason for this low DRE is not apparent, particularly because good DRE was observed for the low CFC-12 feed concentration test condition. It is generally recognized, however, that high DREs are easier to achieve at higher feed concentrations. An analytical error is not suspected as the measured concentrations of the separately collected duplicate samples agreed well. However, a sampling contaminant is plausible. Similar concentrations of CFC-11 were measured in the CFC-12 incineration test samples. Lesser concentrations of CFC-11 were also present in the No. 2 oil baseline test samples. Trace quantities of CFC-11 were also present in the nitrogen blanks.

The addition of water to the combustion chamber to control burner temperature may also enhance the thermal destruction of CFCs. The addition of water would result in an increase in hydroxyl (OH) radicals. The OH radicals provide a bimolecular destruction mechanism in addition to unimolecular bond rupture decomposition.[10] In a turbulent flame reactor, Pedersen and Källman have demonstrated that larger amounts of CFCs can be thermally destroyed with the addition of steam.[11]

The volatile organic PICs screen results are presented in Table III. The "less than" concentrations presented are based on analyte practical quantitation limits (PQLs). Very few PICs were present in the baseline, low CFC-12 feed concentration, and low CFC-11 feed concentration test conditions. Many of the PICs present were at or near PQLs. The CFC-11 high feed concentration test condition did reveal a number of PICs in substantial concentrations. Chloroform was present at a relatively high concentration (1,500-1,600 $\mu g/m^3$). Carbon tetrachloride was also emitted but at a much lower concentration (170 $\mu g/m^3$). It has been shown that PICs resulting from the thermal decomposition of chlorinated organic compounds favor the formation of unsaturated chlorine and single carbon chlorine compounds.[12]

TABLE III. VOLATILE ORGANIC PIC DATA SUMMARY

Test Condition	Test 1		Test 2		Test 3		Test 4	
Concentration	No. 2 Fuel Oil Blank $\mu g/m^3$		CFC-12 Low Feed $\mu g/m^3$		CFC-11 Low Feed $\mu g/m^3$		CFC-11 High Feed $\mu g/m^3$	
Sample	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
Compound								
Dichlorodifluoromethane	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Chloromethane	< 10	< 10	220	< 10	< 10	< 10	< 10	< 10
Vinyl chloride	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Bromomethane	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Chloroethane	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Trichlorofluoromethane	34	87	270	130	270	290	490	320
1,1-Dichloroethene	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Acetone	52	66	270	110	1300	55	160	410
Methylene chloride	< 10	< 10	18	110	47	< 10	15	23
Trans-1,2-dichloroethene	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
1,1-Dichloroethane	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Chloroform	< 10	< 10	23	89	< 10	< 10	1500	1600
1,1,1-Trichloroethane	33	< 10	13	< 10	28	< 10	< 10	17
Carbon tetrachloride	< 10	< 10	< 10	< 10	< 10	< 10	170	170
1,2-Dichloroethane	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Benzene	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Trichloroethene	80	11	< 10	< 10	< 10	< 10	< 10	< 10
1,2-Dichloropropane	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Bromodichloromethane	< 10	< 10	24	93	< 10	< 10	2000	1300
cis-1,3-Dichloropropene	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Toluene	72	31	350	87	280	1400	150	170
trans-1,3-Dichloropropene	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
1,1,2-Trichloroethane	25	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Tetrachloroethene	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Dibromochloromethane	< 10	< 10	28	< 10	< 10	< 10	2000	1800
Chlorobenzene	< 10	< 10	< 10	< 10	< 10	< 10	15	< 10
Ethyl benzene	< 10	< 10	< 10	< 10	< 10	< 10	36	< 10
Total xylenes	52	25	20	33	70	< 10	250	51
Bromoform	< 10	< 10	18	51	< 10	< 10	1800	2300
1,1,2,2-Tetrachloroethane	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
1,3-Dichlorobenzene	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
1,4-Dichlorobenzene	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
1,2-Dichlorobenzene	< 10	< 10	15	460	< 10	< 10	< 10	< 10

A noteworthy discovery was that several of the PICs present were brominated. Bromodichloromethane, dibromochloromethane, and tribromomethane (bromoform) were the three most prevalent PICs. The presence of these compounds as PICs is supported by the agreement in both the presence and concentration between the duplicate samples. What makes the presence of these PICs surprising is that no source of bromine was apparent in the fuel and/or waste feed. An attempt was made to identify a source of bromine. A sample of the CFC-11 used during testing was collected and submitted for a trace impurities analysis. Although other common CFCs and HCFCs were found at trace levels, no brominated impurities were detected. A sample of the No. 2 fuel oil used during testing was also submitted for analysis. Again, no bromine was detected. Further investigation indicated that brominated compounds had been incinerated in the same test facility in the past. Compounds including dibromofluorobenzene and bromochloropropane had been incinerated. The brominated PICs detected may have resulted from some type of hysteresis effect.

The PCDD/PCDF emissions data are summarized in Table IV. PCDDs and/or PCDFs were detected in all samples collected. However, the mass of PCDD/PCDF material present in most of the test samples was at or near levels present in field blanks. The data are sufficient to provide a quantitative comparison with the PCDD/PCDF emissions data obtained during the initial AEERL-sponsored bench-scale study.[2] This study included a test in which PCDD/PCDF samples were collected while CFC-12 was incinerated at a feed concentration of 8.3 percent (by volume). Total PCDD/PCDF emissions were measured to be 23.80 $\mu g/m^3$, a factor of 100 greater than highest concentration observed for the tests reported here.

TABLE IV. PCDD/PCDF EMISSIONS DATA SUMMARY

Test Condition	Test 1–No. 2 Fuel Oil Baseline				Test 2–CFC-12 Low Feed Concentration			
Sample	(a)		(b)		(a)		(b)	
Cogener	No. Isomers	Conc (ng/m^3)	No. Isomers	Conc (ng/m^3)	No. Isomers	Conc (ng/m^3)	No. Isomers	Conc (ng/m^3)
TCDDs	0	ND	2	13.574	1	0.317	0	ND
TCDFs	0	ND	0	ND	0	ND	0	ND
PeCDDs	0	ND	1	1.232	0	ND	0	ND
PeCDFs	0	ND	0	ND	0	ND	0	ND
HxCDDs	0	ND	2	7.220	0	ND	0	ND
HxCDFs	1	0.352	0	ND	0	ND	1	2.489
HpCDDs	2	2.099	0	ND	2	2.134	0	ND
HpCDFs	1	1.614	0	ND	1	0.901	0	ND
OCDD	1	2.018	0	ND	1	2.485	0	ND
OCDF	0	ND	0	ND	0	ND	0	ND
Total		6.083		22.026		5.837		2.489
	Test 3–CFC-11 Low Feed Concentration				Test 4–CFC-11 High Feed Concentration			
TCDDs	0	ND	7	45.629	2	18.034	0	ND
TCDFs	0	ND	9	44.896	4	77.014	3	96.009
PeCDDs	0	ND	2	2.633	4	11.907	0	ND
PeCDFs	0	ND	0	ND	9	23.251	0	ND
HxCDDs	0	ND	0	ND	1	1.861	0	ND
HxCDFs	0	ND	2	4.913	5	7.700	1	0.822
HpCDDs	0	ND	0	ND	1	0.431	0	ND
HpCDFs	0	ND	0	ND	0	ND	0	ND
OCDD	1	2.183	1	1.706	0	ND	1	2.341
OCDF	0	ND	0	ND	0	ND	0	ND
Total		2.183		99.777		140.198		99.172

ND = Not Detected

It is difficult to determine if PCDD/PCDF concentration is a function of CFC feed concentration. Figure 2 graphically depicts total PCDD/PCDF emissions for each test. It appears that the high CFC-11 feed concentration condition resulted in slightly increased average PCDD/PCDF emissions. There is also better agreement between the duplicate samples collected for this test condition. Because of the large variation in results of the duplicate samples, it is difficult to characterize the CFC-11 low feed concentration test condition. A sampling contaminant is suspected, as similar variation was observed in the field blanks. An analytical contaminant is not suspected because PCDDs/PCDFs were not detected in the laboratory blanks.

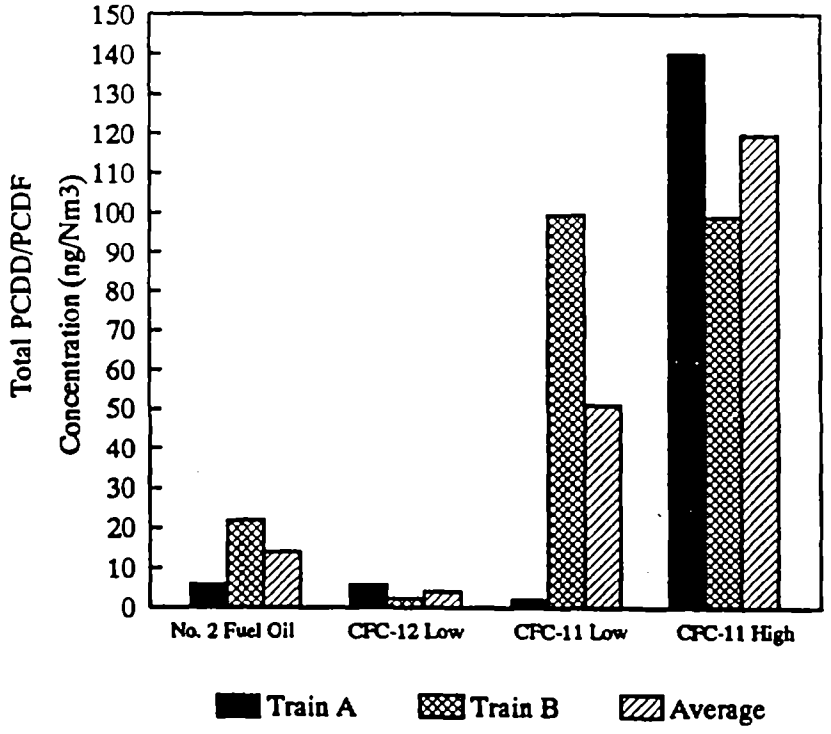

Figure 2. Total PCDD/PCDF emissions for each test condition.

The scrubber water samples were also screened for PCDDs and PCDFs. The scrubber water was targeted for screening because PCDDs and PCDFs possess relatively low vapor pressures and the scrubber water temperature was only about 88 °C (190 °F). Possibly, an equilibrium of condensed PCDDs/PCDFs could be reached in a concentration great enough to be measured by the available screening procedure. This was a relatively important consideration, because the initial AEERL-sponsored study sampled at a location upstream of any pollution control equipment.[2] Sampling upstream of the pollution control equipment was not considered for these tests because of the high acid gas concentration of the incinerator emissions.

Unfortunately, these data also proved to be inconclusive. No PCDDs/PCDFs were detected in the scrubber water before incineration testing, after Test 1, and after Test 3. However, substantial quantities of PCDDs/PCDFs (195.0 ng/L total PCDD/PCDF) were present after Test 2, and to a lesser level (34.8 ng/L total PCDD/PCDF), after Test 4. These results are confounding because no PCDDs/PCDFs were measured after Test 3 but were

measured after Test 2. A definitive explanation is not obvious. The most logical source for this disparity is a sampling or analytical contaminant. However, no contaminant source was isolated.

Semivolatile organic PICs screen results are presented in Table V. Target analytes focused on those compounds considered to be PCDD/PCDF precursors. Only half of the Method 23 samples were analyzed. The majority of the target analytes were not detected. Based on instrumentation detection levels, "less than" emission concentration levels are presented. Bromoform was also tentatively identified in the high CFC-11 feed concentration test condition sample. This serves to further confirm the presence of brominated PICs in incinerator emissions. No semivolatile organic target analytes were detected in the scrubber water samples.

TABLE V. SEMIVOLATILE ORGANIC PIC DATA SUMMARY

	No. 2 Fuel Oil Baseline	CFC-12 Low Feed	CFC-11 Low Feed	CFC-11 High Feed
Target Analyte	Concentration ($\mu g/m^3$)			
1,3-Dichlorobenzene	< 2.5	< 2.3	< 2.4	< 3.2
1,4-Dichlorobenzene	< 2.8	< 2.5	< 2.7	< 3.6
1,2-Dichlorobenzene	< 5.0	< 4.5	< 4.8	< 6.5
1,2,4-Trichlorobenzene	< 3.3	< 2.9	< 3.1	< 4.2
1,2,4,5-Tetrachlorobenzene	< 4.6	< 4.1	< 4.3	< 5.9
2-Chlorophenol	< 9.0	< 8.1	< 8.6	< 11.6
2,6-Dichlorophenol	< 4.2	< 3.7	< 3.9	< 5.3
2,3,4-Trichlorophenol	< 1.4	< 1.3	< 1.4	< 1.8
Pentachlorophenol	< 12.6	< 11.3	< 11.9	< 16.1
1-Chloronaphthalene	< 2.4	< 2.1	< 2.2	< 3.0
2-Chloronaphthalene	< 1.6	< 1.5	< 1.5	< 2.1
Dibenzofuran	< 1.2	< 1.1	< 1.2	< 1.6
Naphthalene	< 1.9	< 1.7	< 1.8	< 2.5
Acenaphthylene	< 0.4	< 0.4	< 0.4	< 0.6
Acenaphthene	< 1.5	< 1.3	< 1.4	< 1.9
Fluorene	< 1.9	< 1.7	< 1.8	< 2.5
Fluoranthene	29.7	< 1.2	< 1.3	< 1.7
Phenanthrene	< 0.8	< 0.7	< 0.8	< 1.0
Anthracene	37.1	< 1.2	< 1.3	< 1.7
Chrysene	< 2.4	< 2.1	< 2.2	< 3.0
Benzo(a)anthracene	< 0.9	< 0.8	< 0.8	< 1.1
Benzo(k)fluoranthene	< 13.8	< 12.4	< 13.0	< 17.7
Benzo(a)pyrene	< 10.1	< 9.1	< 9.5	< 12.9
Indeno(1,2,3-c,d)pyrene	< 16.3	< 14.7	< 15.4	< 20.9
Dibenz(a,h)anthracene	< 12.5	< 11.2	< 11.8	< 16.0
Benzo(g,h,i)perylene	< 23.7	< 21.3	< 22.4	< 30.4
Pyrene	41.5	< 3.3	< 3.5	< 4.7

The absence of chlorobenzenes and PAHs and low PCDD/PCDF concentrations may be attributable to the water injection. During the incineration of CFC-12, Pedersen and Källman determined that the single important chemical factor in reducing the formation of chlorobenzenes and PAHs was the halogen/hydrogen ratio.[11] The increase in available hydrogen resulting from water injection may be sufficient to decrease the ratio to levels where the formation of chlorobenzenes and PAHs is negligible, and since those compounds are suspected precursors for PCDDs and PCDFs, the increase in available hydrogen may have inhibited PCDD/PCDF formation.

CONCLUSIONS AND RECOMMENDATIONS

This study effectively characterized the organic emissions resulting from the pilot-scale incineration of CFCs. CFC-12 and CFC-11 were destroyed/removed at feed concentrations representative of full-scale thermal destruction facilities (2.3 and 2.9 percent, respectively). A high CFC-11 feed concentration condition (68.9 percent) was also evaluated. Greater than 5 nines DRE was observed for the CFC-12 and high CFC-11 test conditions. Only three nines DRE was observed for the low CFC-11 feed concentration test condition.

The presence of volatile and semivolatile organic PICs was screened for. The PIC screens included target analytes such as chlorinated aliphatics, CBs, CPs, PAHs, and PCDDs/PCDFs. Essentially, no target PICs were found for the low CFC feed concentration tests. The high CFC-11 feed concentration test condition PIC screens did indicate that several volatile organic target PICs, as well as several non-target volatile organic PICs, were indeed formed. Chloroform, bromodichloromethane, dibromochloromethane, and bromoform were emitted in substantial concentrations (1,500-2,300 $\mu g/m^3$). Carbon tetrachloride was also generated, but at a lower concentration (170 $\mu g/m^3$). The presence of brominated PICs was particularly surprising, as no source of bromine was readily identifiable; the CFC-11 and fuel oil used during testing were analyzed specifically for trace bromine and found to be free of bromine. Prior tests on the incineration test facility were suspected as the bromine source.

Essentially no semivolatile organic PIC target analytes were detected. This finding is significant in that CBs and PAHs, PICs identified in a bench-scale CFC incineration study, were not detected.

The total PCDD/PCDF emission concentrations measured (2-140 ng/m^3) were a factor of 100 less than those reported in another AEERL-sponsored CFC incineration study,[2] indicating that the formation of PCDDs/PCDFs from the incineration of CFCs may not be as large a concern as was initially suspected. It does appear, however, that increased PCDD/PCDF emissions were realized at the high CFC-11 feed concentration test condition.

The injection of water into the combustion zone to control incinerator temperature may have several benefits. The injection of water may enhance CFC destruction efficiency. Water injection would lead to an increase in the hydroxyl radical population, thereby providing a bimolecular destruction mechanism in addition to unimolecular thermal bond rupture. The injection of water may also reduce the formation of PICs. The injected water also provides an additional source of hydrogen. Hydrogen is involved in reactions that scavenge halogen free radicals. As a result, the addition of water may also have contributed to the low emissions of PCDDs and PCDFs.

Whereas this study was effective in evaluating CFC incineration viability, the study also revealed several additional interesting topics. Specifically, the effect of water or steam addition to the combustion zone as well as the incineration of waste CFCs are not fully understood.

The addition of water to the combustion zone may have a positive effect on both CFC destruction efficiency and PIC minimization. However, it is certainly possible that a large number of incineration facilities do not add water or steam to the combustion zone. It would be interesting to evaluate a high CFC feed concentration without the addition of water or steam.

This study only marginally evaluated the incineration products of two CFCs. Many other CFCs ultimately requiring disposal exist. The CFCs evaluated during these tests were unused, reagent grade products. Waste and recycled CFCs were not examined. Characterizations of combustion products of waste/recycled refrigeration CFCs should be helpful. These products are likely to have had long-term contact with copper tubing. The possibility exists that some copper may have been leached from tubing, particularly if any acids were present. The catalytic properties of copper in PCDD/PCDF formation are well characterized[13,14].

ACKNOWLEDGEMENTS

This study was conducted under EPA contract 68-DO-0141 with Acurex Environmental Corporation. C. W. Lee was the EPA Task Officer. The valuable contributions made by T-Thermal Inc. are also acknowledged.

DISCLAIMER

The contents of this paper should not be construed to represent EPA policy nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

REFERENCES

1. Dickerman, J.C., Emmel, T.E., Harris, G.E. and Hummel, K.E., "Technologies for CFC/Halon Destruction," EPA-600/7-89-011 (NTIS PB90-116955), U.S. Environmental Protection Agency-Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, October 1989.

2. Hassel, G.R., "Experimental Investigation of PIC Formation in CFC Incineration," EPA-600/7-91-010 (NTIS PB92-126952), U.S. Environmental Protection Agency-Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, December 1991.

3. Shaub, W.M. and Tsang, W., "Dioxin Formation in Incinerators," Environmental Science and Technology, 17:721-730, 1983.

4. Method 18, "Measurement of Gaseous Organic Compounds Emissions by Gas Chromatography," in Title 40 Code of Federal Regulations Part 60, Appendix A, U.S. Government Printing Office, Washington, DC, 1991.

5. Method 23, "The Analysis of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Stationary Sources," in Title 40 Code of Federal Regulations Part 60, Appendix A, U.S. Government Printing Office, Washington, DC, 1991.

6. Method 8240, "Gas Chromatography/Mass Spectrometry for Volatile Organics," in Test Methods for Evaluating Solid Waste, Volume IB: Laboratory Manual Physical/Chemical Methods, EPA-SW-846 (NTIS PB-88-239223), 3rd ed., U.S. Environmental Protection Agency, Washington, DC, 1986.

7. Method 8280, "The Analysis of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans," in Test Methods for Evaluating Solid Waste, Volume IB: Laboratory Manual Physical/Chemical Methods, EPA-SW-846 (NTIS PB-88-239223), 3rd ed., U.S. Environmental Protection Agency, Washington, DC, 1986.

8. Method 8270, "Gas Chromatography/Mass Spectrometry for Semivolatile Organics: Capillary Column Technique," in Test Methods for Evaluating Solid Waste, Volume IB: Laboratory Manual Physical/Chemical Methods, EPA-SW-846 (NTIS PB-88-239223), 3rd ed., U.S. Environmental Protection Agency, Washington, DC, 1986.

9. Appendix B to Part 136, "Definition and Procedure for the Determination of the Method Detection Limit-Revision 1.11," in Title 40 Code of Federal Regulations Part 136, Appendix B, U.S. Government Printing Office, Washington, DC, 1991.

10. Graham, J.L., Hall, D.L. and Dellinger, B., "Laboratory Investigation of Thermal Degradation of a Mixture of Hazardous Organic Compounds," Environmental Science and Technology, 20:703-710, 1986.

11. Pedersen, J.R. and Källman, B., "Investigation of the Thermal Destruction of Chlorofluoromethanes in a Turbulent Flame," Chemosphere, 24(2):117-126, 1992.

12. Tsang, W., "Mechanisms for the Formation and Destruction of Chlorinated Organic Products of Incomplete Combustion," Combustion Science and Technology, 74:99-116, 1990.

13. Stieglitz, L., Zwick, G., Beck, J. and Vogg, H., "On the de-novo Synthesis of PCDD/PCDF on Fly Ash of Municipal Waste Incinerators," Chemosphere, 18:1219-1226, 1989.

14. Gullett, B., Bruce, K. and Beach, L., "The Effect of Metal Catalysts on the Formation of Polychlorinated Dibenzo-p-dioxin and Polychlorinated Dibenzofuran Precursors," Chemosphere, 20:1945-1952, 1990.

AEERL-P-1073

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before comple

1. REPORT NO.	2.	3.
EPA/600/A-94/008		

4. TITLE AND SUBTITLE	5. REPORT DATE
Organic emissions from Pilot-scale Incineration of CFCs	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
J. V. Ryan (Acurex), C. W. Lee (EPA/AEERL), and Steven Korn (T-Thermal)*	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Acurex Environmental Corporation P.O. Box 13109 Research Triangle Park, North Carolina 27709	11. CONTRACT/GRANT NO. 68-DO-0141, Tasks 92-081 and 93-149

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
EPA, Office of Research and Development Air and Energy Engineering Research Laboratory Research Triangle Park, NC 27711	Published paper; 1/92-4/93 14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES AEERL project officer is C. W. Lee, Mail Drop 65, 919/541-7663. Presented at 12th Annual Incineration Conference, Knoxville, TN, 5/3-7/93. (*) T-Thermal, Inc., Brook Rd., Conshohocken, PA 19028.

16. ABSTRACT The paper gives results of the characterization of organic emissions resulting from the pilot-scale incineration of trichlorofluoromethane (CFC-11) and dichlorodifluoromethane (CFC-12) under varied feed concentrations. (NOTE: As a result of the Montreal Protocol, an international accord implemented to reduce the production and use of stratospheric ozone depleting substances, considerable quantities of chlorofluorocarbons (CFCs) and halons may be accumulated and ultimately require disposal or destruction. Incineration is a potential destruction technology; however, little is known of the combustion emission characteritics from CFC incineration.) A 293-kW (1 million Btu/h) incinerator was made available to the EPA for the characterization, which focused on determining the destruction efficiencies (DEs) and major products of incomplete combustion (PICs) for each CFC evaluated. Sampling was performed to screen for volatile and semivolatile organic emission products including chlorinated aliphatics, chlorobenzenes, chlorophenols, polychlorinated dibenzodioxins and furans (PCDDs and PCDFs), and polyaromatic hydrocarbons (PAHs). Results indicate that 99.999% DE can be achieved at a CFC-11 feed concentration as high as 69% by mass. The formation of volatile and semivolatile organic PICs was minimal. "Less than" concentrations are presented for target analytes not detected.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Halohydrocarbons	Stationary Sources	07C
Incinerators	Chlorofluorocarbons	
Organic Compounds	Thermal Destruction	
Emission	Destruction Efficiency	14G
Ozone		07B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	Unclassified	
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (9-73)