



## Project Summary

# Experimental Investigation of PIC Formation During CFC Incineration

G. Kryder and B. Springsteen

Experiments were conducted to assess (1) the effect of residual copper retained in an incineration facility on polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/PCDF) formation during incineration of non-copper-containing chlorofluorocarbons (CFCs); and (2) the formation of chlorinated and aromatic products of incomplete combustion (PICs), including PCDD/PCDFs, during incineration of CFC recycling residue and hydrochlorofluorocarbons (HCFCs). High concentrations of PCDD/PCDFs (23,800 ng/dscm at 7% O<sub>2</sub>) measured in a fiscal year (FY) 91 study during incineration of dichlorodifluoromethane (CFC-12) in the turbulent flame reactor (TFR) could not be repeated in the present study. Repetition tests conducted in the same facility under similar operating conditions resulted in PCDD/PCDF concentrations of 118 ng/dscm at 7% O<sub>2</sub>. However, results of the present study suggest that residual copper retained in an incineration facility possibly promotes the formation of PCDD/PCDFs during incineration of CFC-12 which does not contain copper. Tests conducted in the TFR facility resulted in measured PCDD/PCDF concentrations of 386 - 454 ng/dscm at 7% O<sub>2</sub> during incineration of CFC-12 which followed incineration of copper-containing compounds. These results suggest that CFCs may best be incinerated in incinerators that do not treat any copper-containing waste prior to CFC incineration, in order to eliminate the possibility that residual copper retained in the incineration systems could promote PCDD/PCDF formation during subsequent CFC incineration. In this study, 1,1-dichloro-1-fluoroethane (HCFC-141b) and the oily residue generated during CFC recycling processes were thermally destroyed without sig-

nificant emissions of volatile organic PICs and PCDD/PCDFs.

*This Project Summary was developed by EPA's National Risk Management Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

## Introduction

A bench-scale study of the incineration of CFCs, CFC-12 and trichlorofluoromethane (CFC-11), was conducted in FY 91. For tests performed in the TRF, a water-cooled furnace (rated at 20.5 kW) at relatively low flame temperatures (790°C for the primary flame and 980°C for the secondary flame), the CFCs were shown to be consistently destroyed at very high efficiency (greater than 99.999%); however, significant levels of chlorinated and aromatic PICs were detected. The test facility in which the FY 91 tests were conducted was previously exposed to trace metals including copper during incineration of metals-containing waste prior to the CFC incineration study. PCDD/PCDFs were sampled for and detected at high levels during a single test condition in this study. The formation of high levels of PCDD/PCDFs could have been the result of the catalytic effect of residual copper in the test facility remaining after incineration of the metals-containing waste. Of particular concern, PCDD/PCDFs were sampled for and detected at high levels in one test condition.

Subsequently, additional CFC incineration tests were performed in T-Thermal's pilot-scale incinerator (rated at 290 kW) in FY 92. These tests were conducted at a high flame temperature (1,090°C) with water injection into the flame zone for temperature control. PCDD/PCDFs were

found at moderate levels in only one test with a high input of a CFC (69% CFC-11 by weight in fuel oil). PCDD/PCDFs were not found in other tests with lower CFC inputs. The avoidance of PCDD/PCDF formation in these tests is possibly due to the higher temperature and/or water injection. Also, the pilot-scale incinerator is equipped with a water-quench tank directly downstream of the burner to provide rapid flue gas quenching; flue gases were quenched from 1,090 to 120°C in about 0.5 sec. The high flue gas quenching rate may have limited chemical reactions that lead to the formation of PICs in the flue gas.

Follow-up bench-scale tests were conducted in FY 92, using the controlled temperature tower (CTT) to determine the effect of flame zone temperature on gas-phase flame formation and destruction of PICs during CFC-12 incineration. The effect of water injection into the flame zone was also studied. PCDD/PCDFs were not detected at a high flame zone temperature (1,200°C), while moderate levels of PCDD/PCDFs were detected at a lower flame zone temperature (900°C). Low levels of PCDD/PCDFs were also detected at the lower temperature with water injection into the flame zone. Flame zone water injection may have a reducing effect on PCDD/PCDF formation during CFC-12 incineration.

The effect of metal contamination of CFCs on the incineration emissions was studied in FY 93. The CFCs evaluated during all of the previous incineration tests were unused, reagent grade products; waste and recycled CFCs were not examined. CFC refrigerants are likely to have had long-term contact with heat exchangers made of copper-based alloys. The possibility exists that some copper may have been leached from copper alloy tubing by acids which may be formed as the result of a CFC's degradation. The catalytic properties of copper in PCDD/PCDF formation are well documented. Test results indicated that incineration of waste CFC-11 produced low levels of PCDD/PCDFs. Significant levels of PCDD/PCDFs were found when the waste CFC-11 which was tested was spiked with 300 ppm copper.

## Purpose

The purposes of this work were (1) to further evaluate incineration as one of the appropriate technologies for the safe disposal of CFCs, including HCFCs and CFC recycling residues; and (2) to compare current results with those from earlier work in order to determine if the earlier high-

dioxin emission results are typical for CFC incineration or a one-time event. The first objective of this study was to assess the effect of residual copper retained in an incineration facility on PCDD/PCDF formation during incineration of non-copper-containing CFCs. Therefore, initial work of the present study was a repetition of the PCDD/PCDF formation measured in FY 91. This repetition test was performed in the same water-cooled furnace (TFR) at relatively low flame temperatures in which the FY 91 tests were conducted. In fact, the bench-scale test facility was not in use between the FY 91 and the present tests so any residual copper that was present in FY 91 should have been present in FY 94. Subsequent to the repetition test, two additional tests were performed with more copper injected into the TFR prior to the CFC-12 incineration to evaluate the effect of residual copper retained in the TFR on subsequent CFC incineration. At the beginning of the test, copper-containing fuel was incinerated in the test facility, followed by incineration of non-copper-containing CFC-12 during which the emissions of PCDD/PCDFs were measured.

The second objective of this study was to measure the formation of chlorinated and aromatic PICs, including PCDD/PCDFs, during incineration of a CFC recycling residue and a representative HCFC. The production of CFCs is severely restricted under international agreements and federal regulations. HCFCs have become more popular as CFC substitute refrigerants. Incineration may be an appropriate disposal technology for HCFCs. Therefore, in the second part of this study, the formation of PICs and PCDD/PCDFs during incineration of a HCFC was investigated. In addition to substitution of HCFC for CFC, recycling of CFCs is becoming more popular. Significant quantities of residues generated during the recycling process require disposal. Incineration of these residues may be an appropriate disposal method. However, preliminary analysis of CFC recycling residues has shown that they may contain up to 15 ppm copper, which has been shown to have a catalytic effect on the formation of PCDD/PCDFs. Therefore, in the last part of this study, the formation of PICs and PCDD/PCDFs during incineration of a CFC recycling residue was investigated.

## Procedure

All experimental testing was conducted at a test site in Irvine, California. Two bench-scale combustion research facilities were utilized in this study. The experi-

mental tests to assess the effect of residual copper retained in an incineration facility on PCDD/PCDF formation during incineration of non-copper-containing CFCs, including the repetition of the FY 91 tests, were conducted in the TFR used for the FY 91 study. The experimental tests to measure the formation of chlorinated and aromatic PICs, including PCDD/PCDFs, during incineration of a CFC recycling residue and a HCFC were conducted in the CTT used for the FY 92 and FY 93 studies.

The experimental tests in this study consisted of three tasks shown in Table 1. The primary focus of the experimental sampling was the measurement of PCDD/PCDF formation during incineration of CFC, HCFC, and a CFC recycling residue. During each test, flue gas samples were collected for analysis of semi-volatile PCDD/PCDFs using EPA Method 23. During incineration of a HCFC and a CFC recycling residue, flue gas samples were collected and analyzed for volatile halogenated and non-halogenated organic PICs using EPA SW-846 Method 0030 (volatile organic sampling train). Also, the flue gas was monitored for other combustion products (O<sub>2</sub>, CO<sub>2</sub>, CO, and NO) using a continuous emission monitor.

Task 1 was a repetition test of the FY 91 high PCDD/PCDF emission experimental results. The tests were conducted in the TFR. The TFR facility was not used for experimental testing after completion of the CFC incineration study in FY 91; however, the refractory quarl in the primary combustion zone had been replaced. For these tests, the TFR was configured similarly to the FY 91 configuration. The primary combustion zone was maintained at 760 - 870°C, and the secondary was maintained at 980 - 1,090°C. The Task 2 tests were also conducted in the TFR facility which was operated in the same configuration as in the Task 1 tests. Fuel oil containing copper was fired in the facility, and an aqueous solution of copper salt was injected into the facility to simulate incineration of copper-containing wastes. Following this, CFC-12 (~ 9% by volume in propane) was incinerated, and the formation of PCDD/PCDFs in the flue gas was measured at two sampling locations. Additional copper-containing fuel was fired in the facility, and then the CFC-12 incineration test was repeated. Task 3 was designed to measure formation of chlorinated and aromatic PICs, including PCDD/PCDFs, during incineration of a HCFC and a CFC recycling residue.

## Results and Discussion

Task 1 consisted of three repetition tests, Tests 1 to 3 (see Table 1). PCDD/PCDFs were not detected in Test 1, the TFR system blank, indicating no background contamination in the propane fuel, sampling train, recovery agents, or resulting from the analytical procedure. Tests 2 and 3 were conducted under similar conditions as the FY 91 test in which high levels of PCDD/PCDFs were detected. The two tests were conducted on consecutive days under similar facility operating conditions in order to measure the repeatability of the experiment. The high temperature sample (Location 1 at the afterburner outlet) for Test 3 was not analyzed due to loss of sample prior to laboratory analysis. Low levels of PCDD/PCDFs (5.4 ng/dscm) were detected at the high temperature sampling location sample collected during Test 2. The PCDD/PCDF concentrations measured at the downstream sampling location (Location 2) were higher (117.8 ng/dscm for Test 3). However, these measured PCDD/PCDF concentrations were much lower than the high levels measured in FY 91 (23,830 ng/dscm). Excellent combustion conditions were achieved for all test conditions. In all cases, less than 50 ppmv of CO, corrected to 7% O<sub>2</sub>, was detected in the combustion flue gas.

Prior to Task 2, the TFR facility was conditioned by incinerating a copper-containing fuel and by injecting a copper-containing aqueous solution. The copper-containing fuel was fired in the TFR primary combustor, and the copper-containing solution was injected into the primary zone during natural gas combustion. During combustion of the copper-containing fuel and injection of the copper-containing solution, the primary combustion zone of the TFR was fired at approximately 30 kW and the afterburner was not fired.

For Task 2 (see Table 1), Tests 7 and 8 were CFC-12 incineration tests after copper had been added into the test facility. Results show that higher levels of PCDD/PCDFs were formed under these conditions. In Test 7, the PCDD/PCDF concentrations at the afterburner outlet (Location 1) and at the low-temperature sampling location (Location 2) were 118 and 454 ng/dscm, respectively. During Test 8, PCDD/PCDF formation was not quite as high: results indicated 53.8 and 386 ng/dscm for the afterburner outlet and downstream locations, respectively. The major difference between Tests 7 and 8 was the elapsed time between copper injection and CFC-12 incineration which allowed residual copper to be purged from the TFR. Test 7

commenced 3 hours of propane firing after injecting copper into the TFR, while for Test 8, 54 hours of propane firing elapsed following copper injection prior to CFC-12 incineration.

For Task 3, Tests 4 to 6 were conducted in the CTT (see Table 1). Test 4 was a facility system blank in which only propane was fired in the facility. During Test 5, HCFC-141b was incinerated in the facility at a HCFC/propane concentration of 7.4%. Finally, during Test 6, CFC recycling residue was incinerated without any auxiliary fuel. Excellent combustion conditions were achieved for all test conditions, including incineration of CFC recycling residue with no auxiliary fuel. In all cases, less than 35 ppmv of CO, corrected to 7% O<sub>2</sub>, was detected in the combustion flue gas.

Volatile PICs, determined from the EPA SW 846 Method 0030 sampling trains, were measured for Tests 4 to 6. The concentrations of volatile organics in the flue gas for all three tests were very low. During Test 4 (facility system blank), no volatile organic compounds were measured at levels significantly higher than the background levels measured in the field blank. During Test 5 (HCFC-141b incineration), chloroform was measured at an average concentration of 14.5 µg/dscm. The concentrations of acetone and methylene chloride were 67.9 and 129 µg/dscm, respectively; however, the concentrations of these compounds in the associated field blank were nearly the same. During Test 6 (CFC recycling residue incineration), no compounds were measured at significant concentrations. For the analysis in all cases, surrogate recoveries were within acceptable limits.

Test 4 was a facility blank test to measure the background contamination of PCDD/PCDFs during propane combustion in the CTT. A moderate concentration of (~ 3 ng/dscm) PCDD/PCDF was detected in the facility blank test, suggesting background contamination from the propane fuel, sampling train, reagents, or analytical procedure. Duplicate analysis was performed to confirm these facility blank results. The presence of background contamination in the Test 4 measurements suggests that the Test 5 and 6 results may also contain background contamination.

Two Method 23 sampling trains collected samples simultaneously at the downstream sampling location during Test 5. Results of the analysis of these samples indicate PCDD/PCDF concentrations of 2 and 11 ng/dscm for the two samples. These con-

centrations are relatively low compared to those from CFC incineration.

CFC recycling residue was incinerated in Test 6. Two simultaneous Method 23 samples were collected at the downstream sampling location. The concentrations of PCDD/PCDFs during these tests were 52 and 61 ng/dscm. These measured concentrations are similar to those observed from incineration of pure CFCs in the previous study.

Note that the flue gas temperature for Tests 4 to 6 at the Method 23 sampling location (Location 2) was approximately 225°C, which is within the PCDD/PCDF formation "temperature window" of about 200 to 450°C. The residence time between the 1,450°C flame zone temperature and this sampling location was approximately 6.2 sec, more than sufficient time for the *de novo* synthesis of dioxins and furans. However, results from the present study indicate that incineration of HCFC and CFC recycling residue generates very low levels of PCDD/PCDF emissions during this temperature window. The lack of a sufficient level of copper-contaminant present in the HCFC and the CFC recycling residue to promote PCDD/PCDF formation may be the reason for the observed low PCDD/PCDF emissions. Comparable levels of PCDD/PCDF emissions were also observed from incineration of pure CFC-12 in the FY 92 study.

## Conclusions And Recommendations

High concentrations of PCDD/PCDFs (23,800 ng/dscm) measured in a FY 91 study during incineration of CFC-12 in the TFR could not be repeated in the present study. Repetition tests conducted in the same facility under similar operating conditions resulted in PCDD/PCDF concentrations of 118 ng/dscm at 7% O<sub>2</sub>.

Residual copper retained in an incineration facility can possibly promote the emission of PCDD/PCDFs during incineration of CFC-12 which does not contain copper. Tests conducted in the TFR facility resulted in measured PCDD/PCDF concentrations of 386 - 454 ng/dscm at 7% O<sub>2</sub> during incineration of CFC-12 which followed incineration of copper-containing compounds. Previous studies have shown evidence of PCDD/PCDF formation during incineration of chlorinated wastes in the presence of trace copper in systems with sufficient residence time in the PCDD/PCDF temperature formation window. This promotional effect of copper may limit the types of waste materials which can be incinerated prior to incineration of highly chlorinated CFCs. The present results sug-

gest that CFCs may best be incinerated in incinerators that do not treat any copper-containing waste materials prior to CFC incineration, in order to eliminate the possibility that residual copper retained in the incineration systems could promote

PCDD/PCDF formation during subsequent CFC incineration.

Incineration can be used to destroy 1,1-dichloro-1-fluoroethane (HCFC-141b) without generating significant quantities of volatile organic PICs and PCDD/PCDFs.

Incineration can also be used to destroy the oily residue (which contains 3 ppm copper) generated during CFC recycling without generating significant quantities of volatile organic PICs or PCDD/PCDFs.

**Table 1.** Test Matrix

	Test Number	Test Facility	Test Material	PCDD/F Sampling Location 1 # Replicates	PCDD/F Sampling Location 2 # Replicates	CFC/PIC Sampling # Replicates
Task 1	1	TFR	Facility Blank	0	2	0
	2	TFR	CFC-12	1	1	0
	3	TFR	CFC-12	1	1	0
Task 2	7	TFR	Fuel oil doped with Cu followed by CFC-12*	1	1	0
	8	TFR	Fuel oil doped with Cu followed by CFC-12*	1	1	0
Task 3	4	CTT	Facility Blank	0	2	3
	5	CTT	HCFC-141b	0	2	3
	6	CTT	CFC Residue	0	2	3

\* Fuel oil doped with copper was fired in the test facility prior to testing. Immediately following, CFC-12 was incinerated in the facility. Manual sampling for PCDD/PCDF occurred during CFC-12 incineration.

G. Kryder and B. Springsteen are with Energy and Environmental Research Corp., Irvine, CA 92718.

**C.W. Lee** is the EPA Project Officer (see below).

The complete report, entitled "Experimental Investigation of PIC Formation During CFC Incineration," (Order No. PB96-152186; Cost: \$38.00, subject to change) will be available only from

National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
Telephone: 703-487-4650

The EPA Project Officer can be contacted at  
National Risk Management Research Laboratory  
U.S. Environmental Protection Agency  
Research Triangle Park, NC 27711

United States  
Environmental Protection Agency  
National Risk Management  
Research Laboratory (G-72)  
Cincinnati, OH 45268

BULK RATE  
POSTAGE & FEES PAID  
EPA  
PERMIT No. G-35

Official Business  
Penalty for Private Use  
\$300

EPA/600/SR-96/007