



## Project Summary

# Study on Distributions and Recoveries of Tetrachlorodibenzo-p-Dioxin and Octachlorodibenzo-p-Dioxin in a MM5 Sampling Train

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The data from investigations on the distributions and recoveries of spiked 2,3,7,8-tetrachlorodibenzo-p-dioxin-<sup>14</sup>C (TCDD-<sup>14</sup>C) and octachlorodibenzo-p-dioxin-<sup>14</sup>C (OCDD-<sup>14</sup>C) in a MM5 sampling train are discussed in this report. <sup>14</sup>C-dioxin tracers were used to evaluate whole MM5 sampling train recoveries of dioxin and to determine the distribution of dioxins spiked into a sampling train that was concurrently sampling emissions from a burn of either natural gas ("clean" burn) or kerosene ("dirty" burn). The spike tests were made with a pilot-scale furnace constructed and operated in the laboratory. Recovery of <sup>14</sup>C-dioxin from the MM5 sampling train was determined by liquid scintillation spectrometry. The data indicate that the amount of spiked TCDD-<sup>14</sup>C recovered is approximately 85% during a natural gas test and 83% during a kerosene test. The amount of spiked OCDD-<sup>14</sup>C recovered is approximately 88% during a kerosene test. Also, the data indicate that during the kerosene tests OCDD-<sup>14</sup>C is collected primarily in the front half of the sampling train but TCDD-<sup>14</sup>C is often found in the back half of the sampling train, especially in the XAD. During the natural gas tests, TCDD-<sup>14</sup>C is primarily in the XAD. The distribution of the TCDD-<sup>14</sup>C in the kerosene tests was dependent on the rigid operation of the sampling train.

*This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment 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

The Resource Conservation and Recovery Act (RCRA) of 1976 obligates the U. S. Environmental Protection Agency (EPA) to develop regulations and standards to manage the handling of hazardous waste from its initial generation to its final disposal. The Comprehensive Environmental Response Compensation and Liability Act (CERCLA or "Superfund") of 1980 is concerned with abandoned hazardous waste sites and authorizes the EPA to provide for emergency response and cleanup of chemical spills and for the prevention of the release of hazardous substances into the environment. Properly designed and operated hazardous waste incineration systems can attain the 99.99% destruction and removal efficiency required by law <sup>(1)</sup>. The incineration of municipal wastes generates a fly ash that is composed of 75% to 95% inorganic matter in addition to a complex mixture of organic compounds, elemental carbon, and water <sup>(2)</sup>. Polycyclic aromatic hydrocarbons, polychlorinated phenols, polychlorinated biphenyls (PCBs), polychlorinated dibenzofurans (PCDFs), and polychlorinated dibenzo-p-dioxins (PCDDs) have been identified by Eiceman et al. <sup>(3)</sup>, using GC/MS, in fly ash samples collected from municipal incinerators in Japan, Canada, and the Netherlands. Although the distribution of trace organic compounds was quite different in the samples from the different countries,



PCDDs and PCDFs were present in every sample, suggesting that these compounds are formed universally during incineration processes even though the combustible materials and the incineration conditions may vary (3,4). Because of prevalence of PCDDs in fly ash samples from municipal waste incinerators, the suspected toxicity of several of the dioxin isomers, and the apparent variability in recovery efficiency with different procedures or different samples, there is an urgent need to study the factors that affect the collection and recovery of PCDDs from stack-gas emissions.

Currently, several different procedures are being used to sample stack gases and to determine the amount of PCDDs and PCDFs present in the emissions. SW846 Method 0010 and a draft method entitled "Analytical Procedures to Assay Stack Effluent Samples and Residual Combustion Products for Polychlorinated Dibenzo-p-Dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF)," prepared by Group C--Environmental Standards Workshop sponsored by the American Society of Mechanical Engineers, U.S. Department of Energy and U.S. Environmental Protection Agency, September 18, 1984, have been applied to the sampling of stack gases that may contain chlorinated organic compounds, especially PCDDs and PCDFs. Also, SW846 Method 8280 and the above ASME procedures are used to analyze the extracts of the sampling train to quantify the amount of PCDDs and PCDFs. However, recoveries of specific PCDD isomers when spiked into the MM5 sampling trains are sometimes low. These differences may be due to inherent errors in the sampling and analysis methods such as minor fluctuations in the sampling environment, the random distribution of particulate matter, and nonreproducible extraction and cleanup procedures.

This report describes the efforts of Southern Research Institute (SRI) to evaluate and validate the modified EPA Method 5 (MM5) sampling system for dioxins by collecting and recovering TCDD-<sup>14</sup>C or OCDD-<sup>14</sup>C that was spiked into the sampling train during burns made with a pilot-scale furnace. The use of radiolabeled dioxins and liquid scintillation spectrometry is a sensitive and simple method to evaluate each portion of the sampling train for the recovery of dioxin.

### Technical Approach

Data collected in recent years have indicated that the recovery of dioxins from stack effluent is often poor using current

standard methods of analysis. This is particularly true of oil burns, where the soot level is relatively high. A pilot-scale furnace was constructed and operated in the laboratory that allowed the dynamic spiking of <sup>14</sup>C-labeled dioxin into the airstream of a MM5 sampling train. In our initial evaluation of the sampling system, we used a spiking solution of 2,3,7,8-tetrachloro-dibenzo-p-dioxin-Ring-UL-<sup>14</sup>C (TCDD-<sup>14</sup>C) and burned natural gas to simulate a "clean" (almost no soot) burn in the combustion system. Later we converted to kerosene which simulated a "dirty" burn with a high level of soot being generated. Also, we evaluated the sampling system using a spiking solution of octachlorodibenzo-p-dioxin-Ring-UL-<sup>14</sup>C (OCDD-<sup>14</sup>C).

For each spike test, two MM5-sampling trains were setup as described in the ASME's method. A train consisted of a nozzle, probe, filter and filter holder, transfer lines and condenser, XAD-2 resin and sorbent trap, condensate trap, and three impingers. A small hole was drilled into the union of the nozzle and the probe so that a 30-gauge needle could be inserted. Through this site, the spiked dioxin was introduced into the sampling stream. A dual syringe pump was used to inject a small volume of a concentrated spiking solution of dioxin. The union was heated so that the dioxin readily vaporized and mixed with the influent sample gases. In the initial studies, the TCDD-<sup>14</sup>C spiking solution was delivered at 0.083 mL/min for 60 min (4.98 mL, total) and later at 0.062 mL/min for 90 min (5.58 mL, total). These rates and times corresponded to a delivery of 28.5 ng and 31.9 ng of TCDD-<sup>14</sup>C per sampling train. The OCDD-<sup>14</sup>C spiking solution was delivered at 0.062 mL/min for 90 min and gave a delivery of 169 ng of OCDD-<sup>14</sup>C per sampling train.

After the sampling train cooled, the sections were first rinsed with acetone and then with toluene. The rinses from each section of the train were pooled and concentrated. The filter was removed from the filter bell holder and placed in a Soxhlet extraction thimble. Also, the resin was quantitatively transferred to an extraction thimble. In those areas where soot was collected (nozzle and union, probe and front filter bell), following the solvent rinses, the inner surfaces were wiped with pieces of filter paper. The concentrates and their corresponding filter paper wipes were transferred to extraction thimbles. The condensate and the pooled rinses from the rear filter bell, riser, and condenser were concentrated to 1 mL without the need of extraction in a Soxhlet extraction

apparatus. Also, two 5-mL portions of the <sup>14</sup>C-dioxin spiking solution were concentrated to 1 mL. These two concentrates were used as reference standards to calculate the percent recovery of <sup>14</sup>C-dioxin from the sampling train.

A Soxhlet extraction apparatus was used to extract the filter and XAD resin from the MM5 train and the rinse/wipe of other sections of the sampling train where soot was deposited. For LSC, all extracts were concentrated to 1 mL and percent recovery of radiolabeled tracer was determined.

### Results and Discussion

The purpose of this study was to determine the efficiency of collecting and extracting dioxins using the MM5 sampling train method and also, to determine the distribution of the dioxins within the sampling train based on the composition of the stack emission. To keep the variables to a minimum, for each spike test dual MM5 trains were spiked with approximately 5 mL of a standard solution of radiolabeled dioxin to give a target value of 30 ng of TCDD-<sup>14</sup>C or 170 ng of OCDD-<sup>14</sup>C per sampling train.

The combustion system used in this study was designed to accommodate two sampling trains and to produce either a "clean" or "dirty" burn with respect to the amount of soot formed by selecting the appropriate fuel to burn. The sampling ports on the stacks were made close together so that the area of the stack to be sampled would be as similar as possible. The operation of the furnace and the operational conditions of the sampling trains are presented in the report.

The MM5 train was modified at the union between the nozzle and the inlet to the probe to accommodate a 30-gauge needle attached to a 5-mL syringe via an 18 in. tubing. A syringe pump was set up to hold two syringes so that identical amounts of spiking solution would be delivered to each sampling train. By introducing the spiked dioxin at the nozzle-probe union of the sampling train instead of the furnace or stack, variables limited to the sampling train and analytical procedures could be evaluated. The use of dual spiking trains and delivery of identical spiking solutions at the same rate and amount minimized the variables not associated with the sampling train.

A total of 13 spike tests were conducted in this study. In 10 of the tests TCDD-<sup>14</sup>C was spiked into the sampling train and in the remaining 3 tests OCDD-<sup>14</sup>C was spiked into the sampling train. Four of the TCDD-<sup>14</sup>C spike tests were natural gas tests and six were kerosene tests. All of

the OCDD-<sup>14</sup>C spike tests were kerosene tests. A summary of the spike tests and operational conditions are given in the report.

The spike tests represented two extreme conditions. One, a natural gas test in which no or very little soot or carbon particles are produced and the other one, a kerosene test that produces a dense soot.

The appearance of the components of the sampling train was noticeably different with the two types of combustion conditions. Following a natural gas test, the filter had no visual evidence of soot. However, after a kerosene test, the filter was black with soot and a small amount of soot was also deposited in the sampling probe and the front filter bell holder.

One of the objectives of this study was to evaluate the effect of the combustion fuels on the distribution of dioxins in the sampling train. A trend was found that suggests the use of kerosene causes a slight shift of the distribution of TCDD from the XAD toward the front of the train. The distribution of OCDD in the kerosene tests was almost totally limited to the front half of the sampling train. The shift of distribution to the front half of the train was probably due to the adsorption of dioxin on the soot which was collected in the probe or on the filter. The distribution shift of TCDD was not as extreme as that of OCDD, probably because of a lower vapor pressure of TCDD.

Because soot particulates were deposited throughout the front portion of the sampling train, those areas after several rinses with acetone and toluene were wiped with filter paper. The filter paper and the concentrated rinses were combined in a glass extraction thimble in a Soxhlet apparatus. Extraction with tolu-

ene was allowed to proceed for 16 hours. The XAD-2 resin and the filter from the sampling train were also extracted in a Soxhlet apparatus. However, the rinses from the back portion of the sampling train and the aqueous condensate were concentrated and solvent exchanged into 1-mL of toluene prior to LSC.

Recovery of TCDD-<sup>14</sup>C or OCDD-<sup>14</sup>C was based on the ratio of the total activity (pCi) of the dioxin in the concentrated extract from a specific region of the sampling train to the total activity of dioxin spiked into the sampling train. A summary of the recovery of the <sup>14</sup>C-dioxins and their distribution in the sample train are given in Tables 1 and 2.

### Conclusions

If trace compounds in complex stack emissions from combustion plants are to be accurately determined, appropriate sampling procedures must be selected and carefully followed by the sampling crew. The techniques described in this report demonstrate that the MM5 train can be spiked during its operation, the spiked materials can be recovered, and the overall recovery of the spiked <sup>14</sup>C-dioxins can be determined by liquid scintillation counting. The results of this study indicate that the distribution of dioxins in the sampling train is dependent on the amount of carbon generated in the incineration process and that the distribution of TCDD-<sup>14</sup>C or OCDD-<sup>14</sup>C differs as a function of the temperature of the various regions of the sampling train and the stack gas sampling rate. The data indicate that the amount of spiked TCDD-<sup>14</sup>C recovered was approximately 85% during the natural gas test and 83% during the kerosene tests. The amount of spiked OCDD-<sup>14</sup>C recovered was approximately 88% during the kero-

sene tests. Also, the data indicate that OCDD-<sup>14</sup>C is limited to the front half of the sampling train during the kerosene tests. TCDD-<sup>14</sup>C was often found in the rear half of the sampling train, especially in the XAD of the sampling train during the natural gas tests and the kerosene tests but the distribution of TCDD-<sup>14</sup>C shifted towards the front half of the sampling train in the kerosene tests. In all spike tests, very little, if any, dioxin was found in the condensate. In the natural gas tests, the largest amount of TCDD-<sup>14</sup>C was found in the XAD-2 resin as long as the front half of the sampling train is uniformly heated. A comparison of results of the natural gas tests with that of the kerosene tests, indicates that the distribution of the dioxin is not only dependent on the temperature of the various regions of the sampling train but also the association with the soot particulates deposited in the train.

### References

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Table 1. Summary of Recoveries from MM5 Sample Train Spiked with TCDD -<sup>14</sup>C (90-Min Sampling Time)

Sample	Recovery, %				
	Natural gas		Kerosene tests		
	Test 8A	Test 8B	Test 12B	Test 13A	Test 13B
Nozzle/Union	4.8	3.7	2.7	2.7	3.9
Probe/Front Filter Bell	0.7	0.9	0.5	1.0	1.1
Filter	3.0	1.6	10.4	10.3	9.1
Riser/Condenser/Rear Filter Bell	6.3	25.2	17.0	25.6	22.4
XAD	67.5	54.8	46.2	58.7	38.6
Condensate	0.6	1.2	0.0	0.0	0.1
	83.0	87.5	76.9	98.2	75.2

**Table 2. Summary of Recoveries from MM5 Sample Train Spiked with OCDD-<sup>14</sup>C (90 Min Sampling Time)**

Sample	Recovery, %				
	Test 9B	Test 10A	Test 10B	Test 11A	Test 11B
Nozzle/Union	54.9	11.7	39.0	2.9	54.5
Probe/Front Filter Bell	7.1	58.2	19.9	39.7	26.1
Filter	18.7	21.8	27.5	44.2	8.7
Riser/Condenser/Rear Filter Bell	0.2	0.1	0.1	0.5	0.3
XAD	1.0	0.3	0.3	0.6	0.2
Condensate	0.1	0.0	0.0	0.0	0.0
	81.8	92.1	86.7	87.8	89.8

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The complete report, entitled "Study on Distributions and Recoveries of Tetrachlorodibenzo-p-Dioxin and Octachlorodibenzo-p-Dioxin in a MM5 Sampling Train," (Order No. PB91- 181 743/AS; Cost: \$17.00 subject to change) will be available only from:

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