



## Project Summary

# Efficiency of Dioxin Recovery from Fly Ash Samples During Extraction and Cleanup Process

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The data from investigations of the efficiency of dioxin recovery from fly ash samples during sample extraction and subsequent column cleanup of sample extracts are discussed in this report. Each step of the extraction and the column cleanup procedures was evaluated by using radiolabeled  $^{14}\text{C}$ -dioxins as tracers. Sample extracts and eluate fractions were analyzed by liquid scintillation counting (LSC) and the results confirmed by gas chromatography/mass spectrometry (GC/MS). Recovery data of spiked 2,3,7,8-tetrachlorodibenzo-p-dioxin- $^{14}\text{C}$  (TCDD- $^{14}\text{C}$ ) and octachlorodibenzo-p-dioxin- $^{14}\text{C}$  (OCDD- $^{14}\text{C}$ ) in carbon-free fly ash and fly ash containing from 0.1 to 10% carbon are discussed. The data indicate that the amount of carbon in the fly ash may affect the efficiency of dioxin recovery. Also, procedural details and analytical techniques are extremely important in the quantification of PCDDs and PCDFs.

*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

Currently, several different analytical procedures are being used for the extraction, cleanup, and analysis of PCDDs and PCDFs (1, 2). RCRA Method 8280 and ASME's draft method entitled

"Analytical Procedures to Assay Stack Effluent Samples and Residual Combustion Products for Polychlorinated Dibenzo-p-Dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF)," have been applied to fly ash samples for the determination of PCDDs and PCDFs. Using these procedures, significantly different levels of PCDDs and PCDFs have been found in similar fly ash samples. These differences may be due to changes in combustion parameters or inherent errors in the analysis methods such as nonreproducible extraction and cleanup procedures. Many investigators (3, 4, and 5,) have noted differences in the apparent recovery efficiencies of dioxin by different extraction procedures.

The sorptivity of different fly ash samples for organic compounds in general has been shown to vary greatly. Studies with  $^{14}\text{C}$ -labeled PAHs as radiotracers demonstrated that the extraction recoveries of PAHs from fly ash are inversely proportional to the number of rings in the PAH molecule and that aromatic compounds are more strongly adsorbed than aliphatic hydrocarbons (6). These results indicate that analyses of some fly ash samples for PCDDs and PCDFs may be seriously biased if not corrected for extraction recoveries or sorptivity losses as the concentration levels of PCDDs/PCDFs decrease, the number of chlorines added to the ring structures increases, or the nature of the fly ash changes.

This report describes an effort to evaluate various extraction techniques to remove dioxins from fly ash and to clean-up sample extracts by column chromatography. General chromatographic media and eluting solvents

were evaluated. Each step in the sample preparation was evaluated by using <sup>14</sup>C-radiolabeled 2,3,7,8-tetrachlorodibenzo-p-dioxin and octachlorodibenzo-p-dioxin as tracers. Radiolabeled dioxins allowed the analyst to stop and evaluate each step of the procedure, each extract, and each column eluate fraction by liquid scintillation counting. To validate the radioassay, dioxin was confirmed by gas chromatography/mass spectrometry.

### Technical Approach

A single source of fly ash that was generated from a medium-sulfur, bituminous coal was used in this study. The carbon content of the fly ash was 5%. A carbon-free fly ash was prepared by heating the native fly ash for 16 hours in a muffle furnace set at 750°C. Fly ash samples were spiked with either 2,3,7,8-tetrachlorodibenzo-p-dioxin-Ring-UL-<sup>14</sup>C (TCDD-<sup>14</sup>C) or octachlorodibenzo-p-dioxin-Ring-UL-<sup>14</sup>C (OCDD-<sup>14</sup>C). Also, fly ash samples were spiked with carbon which came from three commercial sources.

The samples were extracted with a Soxhlet extraction apparatus. Fly ash samples (10 g) in the extraction thimbles were spiked with either TCDD-<sup>14</sup>C (88.5 ng; 9,145 pCi) or OCDD-<sup>14</sup>C (230 ng; 10,304 pCi). Extraction times were either 24 or 48 hours, and the extracting solvents were 150 mL of methylene chloride or toluene. Also, some samples were extracted sequentially with methylene chloride followed by toluene.

Three types of chromatography media were used in the column cleanup procedures (basic alumina, AG10; silica gel, Bio-Sil A; and a mixture of activated carbon, AX-21 grade/Celite 545).

The selection of these columns and solvents was based on the recommendations of the ASME's analytical procedures to assay stack effluent samples for PCDDs and PCDFs. All eluate fractions were either saved or solvent exchanged with toluene or n-nonane and submitted for liquid scintillation counting (LSC) and, in some cases, were analyzed by gas chromatography/mass spectrometry.

### Results and Discussion

In this study, radiolabeled TCDD-<sup>14</sup>C and OCDD-<sup>14</sup>C with liquid scintillation counting (LSC) were used to trace the PCDDs through each of the steps associated with an analytical method based on ASME's analysis of stack effluents from combustion processes. The quantification of TCDD-<sup>14</sup>C and OCDD-<sup>14</sup>C by LSC allows for lower

detection limits than does quantification by GC/MS. Also, the use of radiolabeled PCDD is more time and cost effective because separation from impurities (those not radiolabeled) is relatively unimportant, especially in preliminary screening or evaluation of analytical procedures.

### Soxhlet Extraction

Three types of fly ash samples were prepared from a single source of fly ash for this investigation: native fly ash, zero-carbon fly ash, and carbon-spiked fly ash. Elemental analysis of the native fly ash indicated the presence of approximately 5% carbon (wt/wt). Both the native fly ash and the zero-carbon fly ash were spiked with various amounts of carbon. Thus, fly ash samples containing from 0% to 10% carbon (wt/wt) were extracted for 24 hours with methylene chloride followed by an additional 24 hours with toluene or were extracted with only one of the two solvents for 24 hours. The recovery efficiencies for TCDD-<sup>14</sup>C from fly ash spiked at 8.85 ppb and for OCDD-<sup>14</sup>C from fly ash spiked at 23.0 ppb indicate that the carbon content of the fly ash and the nature of the carbon may affect the extraction efficiencies of PCDDs if methylene chloride is used as the extracting solvent in the Soxhlet extraction procedure. Also, the data demonstrate that the recovery of OCDD-<sup>14</sup>C with toluene was less than that of TCDD-<sup>14</sup>C.

### Column Cleanup Chromatography Methods

When dioxins and furans are determined at parts per trillion levels (ppt), concentration of the sample extract is required and extensive sample preparation procedures are needed. This is due to the increased ratio of interfering substances to the compounds of interest in the concentrated extract. Many environmental samples, after they undergo an initial extraction or separation such as liquid-liquid or liquid-solid extraction may require one or more column chromatography cleanup procedures.

The selected column cleanup procedures, as individual columns and as columns in sequence, were evaluated with TCDD-<sup>14</sup>C and OCDD-<sup>14</sup>C. The elution sequences that were used for TCDD-<sup>14</sup>C were based on the ASME's procedures. However, difficulties were noted and several changes were made when we evaluated the cleanup procedures for OCDD-<sup>14</sup>C. A 5 mL

standard of TCDD-<sup>14</sup>C (88.5 ng) or OCDD-<sup>14</sup>C (230 ng) was solvent exchanged into either toluene (n-nonane was used with OCDD-<sup>14</sup>C) or hexane and was concentrated to 1 mL. The resulting concentrate was applied to the appropriate column.

The amounts of TCDD-<sup>14</sup>C recovered in each fraction for the various cleanup steps are summarized in the report. Approximately 80% or more of the TCDD-<sup>14</sup>C was recovered or was accountable. However, several potential problem areas were noted. Over 70% of the TCDD-<sup>14</sup>C immediately eluted from the silica gel column in the first 10 mL of hexane. If the analyst is not aware of this, a major portion of the dioxin may be lost. Thus, all effluent from the silica gel column should be collected, pooled, and concentrated to 1 mL. The data indicate that about 90% of the TCDD-<sup>14</sup>C was recovered from the silica gel column.

Nonpolar polychlorinated compounds will be absorbed on the basic alumina column; thus, this column is often used as a second step in the cleanup procedure. Also, this column allows for the separation of PCBs from dioxins. Approximately 90% of TCDD-<sup>14</sup>C was associated with the 15% methylene chloride in hexane fraction. This step must be monitored closely because the activity and uniformity of the alumina may vary with each lot and some of the dioxin may elute in the 8% methylene chloride in hexane fraction.

If additional cleanup is required on a sample extract, the carbon/celite column may be used. Chlorinated dibenzo-p-dioxins are initially adsorbed on this column and the interferences are removed by eluting with solvents of increasing polarity. The PCDDs can then be backwashed from the column by inverting the column and eluting with toluene. The analyst must monitor this procedure carefully. Approximately 20% of TCDD-<sup>14</sup>C may be lost if a second 4-mL portion of toluene were not collected.

After evaluating the column cleanup procedures using TCDD-<sup>14</sup>C, we made a few modifications in the cleanup procedures. The report gives details of the modifications and the effect on recovery efficiency of dioxin. Also, we increased the volume of toluene from 4 mL to 10 mL as the last step of the AX-21 Carbon/Celite 545 cleanup procedure. Because the first two fractions collected from this column in our initial evaluation were free of TCDD-<sup>14</sup>C, the 1 mL of hexane wash was combined with the 2 mL of 50% methylene chloride in hexane wash.

The total recovery or accountability of OCDD-<sup>14</sup>C varied from 40 to 100%, and >95% of the spiked OCDD-<sup>14</sup>C was recovered from the silica gel column.

The cleanup procedures for OCDD-<sup>14</sup>C with the basic alumina column were identical with those used for TCDD-<sup>14</sup>C. Although a small amount, if any, of OCDD-<sup>14</sup>C remained on the column, the elution with 10 mL of 8% methylene chloride in hexane did contain various amounts of the OCDD-<sup>14</sup>C. If this fraction were discarded, >20% of OCDD-<sup>14</sup>C may be lost.

The cleanup procedures for OCDD-<sup>14</sup>C with the AX-21 Carbon/Celite 545 retained various amounts of the spiked standard. Approximately 80% of the spiked OCDD-<sup>14</sup>C was recovered.

Although we made a few changes in the ASME's cleanup procedures, the evaluation of these changes with OCDD-<sup>14</sup>C revealed additional areas for possible problems. A major concern is the possible loss of dioxins, especially those that are highly chlorinated, during the basic alumina column cleanup procedure.

In an attempt to reduce the amount of OCDD-<sup>14</sup>C eluted from the basic alumina column with 10 mL of 8% methylene chloride in hexane, we changed to 10 mL of 5% methylene chloride in hexane. About 3% of OCDD-<sup>14</sup>C eluted with the 5% methylene chloride in hexane fraction. This is a problem that may not be easily resolved. Certainly this fraction must be analyzed for the presence of trace amounts of dioxins, especially those that are highly chlorinated and when recovery of surrogate standards are low. The results obtained in one study demonstrate another problem that must be addressed. The technical skills and experience of the analyst may bias the data. We recommend that the procedures in this report be implemented by or under the close supervision of analysts with considerable experience in trace analyses.

## Gas Chromatography/Mass Spectrometry

Confirmation by GC/MS was used to validate the data in this report. The presence of TCDD was confirmed by GC/MS. Replicate fly ash samples were carried through the Soxhlet extraction procedures. After the extracts were concentrated to 1 mL, some of the samples were submitted for LSC while others were submitted for GC/MS analysis. LSC indicated that approximately 93% of the labeled material was recovered. The recovery of 2,3,7,8-TCDD, as determined by GC/MS, was 91%.

## Conclusions

If trace compounds in complex environmental samples are to be accurately determined, appropriate analytical procedures must be selected and carefully followed by the analyst. The extraction and cleanup procedures used in the analyses of fly ash for the determination of PCDD and PCDF must be validated by the laboratory and the individual analyst performing the analysis. Laboratory control samples (spiked matrix samples) must be carried through the entire analytical method, which includes sample preparations, cleanup of sample extracts, and instrumental analysis. Procedural details and analytical techniques, such as the cycling of solvent in the Soxhlet extractor, transfer of the solutions, the exchange of solvents, the packing of the chromatographic media into columns, and the volume and composition of the extracting solvents, are extremely important. Variable loss of dioxins can occur in each of these steps. All extracts, eluate fractions, and residues generated during an analysis need to be saved for additional analysis when the recovery of spiked standards or surrogate standards are extremely low in the initial analysis. If there is a question about low recovery after the final eluate is analyzed, the

other eluates may have to be analyzed. With every set of samples that are analyzed, laboratory control samples, surrogate spiking standards, replicate analyses, and method blanks must be included. The extraction and cleanup procedures to determine dioxins in fly ash samples must be implemented by or under close supervision of analysts with experience in trace analyses.

The carbon content of fly ash and the nature of the carbon may affect the extraction efficiency of dioxin. As the carbon content of fly ash increased, the efficiency of spiked TCDD-<sup>14</sup>C and OCDD-<sup>14</sup>C recovery decreased. Modification and control of the extraction and cleanup procedures improved the efficiency of dioxin recover from the fly ash samples.

## References

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*The complete report, entitled "Efficiency of Dioxin Recovery from Fly Ash Samples During Extraction and Cleanup Process," (Order No. PB90-183 393 /AS; Cost: \$15.00 subject to change) will be available only from:*

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