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PROGRESS REPORT:

Determination of Chlorinated Combustion Products in Samples
from a Contaminated Office Building

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Abstract

This report describes additional work that has been completed relevant to the analysis of materials from the Binghamton State Office Building since the March, 1982 document titled "Determination of Polychlorinated Dibenzofurans in Soot Samples from a Contaminated Office Building."¹ Spiked recovery experiments as well as repeat analyses for polychlorinated dibenzofurans (PCDFs) and isomer specific analysis for 2,3,7,8 Tetrachlorodibenzo-p-dioxin (TCDD) in some of the original soot samples have been completed. Improvements in data processing techniques and statistical evaluation of the early high resolution scanning data are discussed. Results are presented from an experiment to measure volatilization rates of TCDD into air and the effectiveness of trapping the vapor on activated silica gel sampling cartridges.

Introduction

The analysis of a series of soot samples taken from various floors of the Binghamton State Office Building has already been described.¹ A number of plausible but experimentally verifiable assumptions were made during the interpretation of this data. These include the hypothesis that Tetra CDF recoveries are generally comparable to those of more highly chlorinated PCDFs, that benzene is an effective extraction solvent, that the precision of these analyses was sufficient to permit sample to sample comparison, and that the signals used in quantitation were entirely due to PCDFs. Results of experiments designed to test these assumptions are presented here. In addition, efforts to further characterize the concentrations of additional compounds present in the soot extract are described. Finally, the results of preliminary experiments designed to develop a well-validated methodology for determination of PCDDs and PCDFs in air at the pg/M^3 level are presented.

1) Recovery of Spiked Soot Samples.

Four 10 milligram samples of carbon (active coconut charcoal) were spiked with labelled and unlabelled standards and subjected to the extraction and clean-up procedures already described. Results are presented in Table 1 for the recovery of Tetra CDF and Hexa CDF. Sample S-2 was spiked with only unlabelled standard (2 ng of Tetra CDF and 13.4 ng of Hexa CDF). Carbon samples S-3, S-4 and S-5 were, in addition, fortified with 95.2 ng of ^{37}Cl -TCDF. Generally, recoveries were good showing that extraction and clean-up were effective and confirming the earlier assumption that ^{37}Cl -Tetra CDF recoveries gave reasonable estimates for Hexa CDF recoveries when Tetra-CDF recoveries were good. The poor recovery (3%) for Tetra CDF in S-5 was also seen in the 12th Floor sample and results from the critical nature of one of the steps of the clean-up procedure.

2) Comparison of the Efficiencies of Benzene and Toluene Extractions

Published data indicates that toluene soxhlet procedures produce superior recoveries from certain matrices.² Since benzene has been used in these studies, a comparison of the extraction efficiencies of these two solvents was appropriate. Table 2 presents recovery data and quantitation of PCDFs in the soot homogenate following the two different extraction procedures. The only difference in the procedures was the substitution of toluene for benzene in the first extraction step. Results show a near equivalent extraction efficiency for PCDFs and, additionally, provide a measure of the reproducibility of the overall analysis procedure.

3) Standard Response Factors.

Several additional standards have been analyzed by GC/MS to obtain response factor so that further quantitations can be made on soot sample extracts. Solutions of a tetrachlorobiphenylene (Tetra CBP) and octachlorobiphenylene (Octa CBP) have been analyzed and response factors for each have been computed. Tetra CBP gave a response factor of 619 counts/ng and Octa CBP 263 counts/ng using nominal concentrations for the available standard solutions. The concentrations of these standards have yet to be accurately established.

An EPA standard Halowax 1051 was also analyzed and found to contain only Hepta and Octa Chloronaphthalene. The standard contained 92% Octachloronaphthalene which gave a response factor of 592 counts/ng of standard injected on-column. These response factors can be used in the quantitation of soot extracts once recoveries for these compounds have been established.

4) Chloronaphthalene Quantitation.

Quantitation of Chloronaphthalenes in the soot homogenate sample has been made based on the response obtained for a Halowax 1051 standard. Assumptions made in this quantitation that are the recovery of these compounds is comparable to that of the PCDFs and that response factors of the congeners are related to the response factors of the PCDF congeners. Based on the Halowax 1051 standard response for Octachloronaphthalene and the recovery of ³⁷Cl-TCDF, the concentration of Chloronaphthalenes in the soot homogenate is as follows:

Polychloronaphthalenes (ppm) in soot
(corrected for recovery)

Tetra-CN	37
Penta-CN	143
Hexa-CN	176
Hepta-CN	105
Octa-CN	11

5) Repeat Analyses

To investigate the reproducibility of the methodology three of the original soot samples were reanalyzed. The results of these analyzes are shown in Table 3. A reproducibility figure was generated by averaging the per cent variation from the mean of each set of two values. The results for TCDF in the soot was calculated using an internal standard and exhibit better reproducibility (15%). The same $^{37}\text{Cl}_4$ -TCDF standard solution was used for both the original and the reanalysis. The concentration of HXCDF and OCDF were calculated by an external standard method using different standard solutions and they are less reproducible. The reproducibility of the method should increase as the availability and amount of the labelled and native PCDFs and PCDDs improves.

6) Mass Assignment in High Resolution Scanning Experiments.

High resolution mass spectrometry permits the assignment of elemental compositions to each resolved measured exact mass in each high resolution mass spectrum. The certainty of structural assignments and quantitation of concentration levels are improved by this technique.

In this phase of the Binghamton work we have analyzed more carefully our high resolution data for accuracy of mass assignment. Table 4 compares the accuracy of mass assignment in a standard injection and three samples of soot taken from the BSOB. The average error and standard deviation of the standard injection run on the same day as the samples and the sample injections are similar and within one standard deviation of the mean. This suggests that the signals used to quantitate these compounds are entirely due to these compounds and not to interferences.

7) Air Sampling for 2,3,7,8 TCDD

In order to extend our 2,3,7,8-TCDD analytical method to air analysis in the Binghamton State Office Building, experiments using ^{14}C radiolabeled 2,3,7,8-TCDD have been performed to investigate TCDD volatilization, trapping efficiency, and breakthrough. Results obtained under laboratory conditions show that 60-70% of a 2 ng. TCDD standard is volatilized from the surface of a quartz-glass tube held at 150°C for 10 min while being swept by air (23°C inlet temp, 37°C outlet temp) at 20 L/min. The volatilized TCDD can then be trapped by an activated silica gel cartridge with a trapping efficiency found to be 80-96% (80% = 72 hr breakthrough study). Experiments are underway to test the use of a glass fiber prefilter to trap air-borne particulate matter separately.

8) Analysis for 2,3,7,8-TCDD.

Three soot samples were analyzed for 2,3,7,8-TCDD after isomer specific clean-up described elsewhere.⁴ The mass

spectrometer was used in the High Resolution Multiple Peak Monitoring (HRMPM) mode to enable the most sensitive detection of 2,3,7,8 TCDD to be made. Signal measurements were taken in the mass region about each of the selected ions in the parent cluster for 2,3,7,8 TCDD and labelled ^{13}C -TCDD so that exact mass chromatograms of native TCDD and internal standard TCDD could be obtained after the samples were run by this GC/MS technique. The quantitations from this analysis are given in Table 5. The concentrations of 2,3,7,8 TCDD found in the soot confirm the finding of other laboratories that the 2,3,7,8 TCDD/2,3,7,8 TCDF ratio is the order of .01 and supports the assumptions used in discussions of chemical and biological data.³

CONCLUSIONS

Data presented for spiked sample recoveries indicate that comparable recoveries are obtained for Tetra CDF and Hexa CDF and thus earlier quantitations based on this assumption have been shown to be valid. The extraction efficiency of benzene has been shown to be comparable to toluene for the analytes of interest. Repeat analyses of several soot samples have indicated that good precision is obtained and that sample to sample comparisons are valid. Evaluation of accurate mass assignments of both sample and standard runs by the high resolution mass spectrometer system form a basis for proving that interferences were not present or were resolved from the signals produced for PCDFs and that valid quantitation was obtained from these data. Additional quantitation of 2,3,7,8 TCDD and preliminary data for PCNs add to the characterization of the soot samples. TCDD levels found were consistent with earlier data and predicted levels.

The preliminary experiments on volatilization and trapping of TCDD in air show analytical promise and will be further evaluated and validated for PCDF and PCDD determinations in air at the pg/M^3 levels.

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TABLE 3

Re-analysis of Soot Samples

Sample #	Series ¹	Concentration (ppm) ³			Recovery % ²
		TCDF	HxCDF	OCDF	
715 9th Floor	1	320	290	35	49
	2	310	197	74	21
713 8th Floor	1	70	32	3.0	50
	2	36	19	4.0	51
Soot Homogenate	1	100	70	4	17
	2	92	44	16	48

¹Series 1 analyzed 3/82, Series 2 10/82.

²Based on ³⁷Cl-TCDF internal standard.

³Values corrected for recovery.

TABLE 4

Comparison of Mass Accuracy Errors

Injection Description Theoretical Masses of Interest	Standard Errors (ppm)	8th Floor	9th Floor	Soot
		713 (Standard Deviation of Error, ppm)	715 (Standard Deviation of Error, ppm)	Homogenate ¹ (Standard Deviation of Error, ppm)
371.8237)	-6 (11)	-7 (13)	-4 (14)	-2 (10)
373.8207) HxCDF	-3 (7)	-4 (13)	-7 (12)	-2 (10)
375.8178)	0 (13)	-6 (10)	-9 (12)	-2 (9)
441.7428)	-3 (14)	-8 (13)	-5 (9)	-2 (14)
443.7398) OCDF	0 (9)	-1 (12)	-7 (14)	-3 (15)
445.7369)	0 (9)	1 (8)	-7 (16)	-5 (10)

¹Soot Homogenate used in Animal Toxicology Studies.

TABLE 5

Analysis of Soot Samples for 2,3,7,8 TCDD

<u>Sample</u>	<u>Conc. (ppm)</u>	<u>RRT</u>	<u>D.L. (ppm)</u>	<u>320/322 Ratio</u>	<u>% Recovery</u>
Soot Homogenate ¹ (floor 3-4)	.46	1.0	.05	86%	7.0
713 (8th floor)	.26	1.0	.03	80%	16
715 (9th floor)	2.2	1.0	.15	69%	8%

¹Soot Homogenate used in animal toxicology studies.