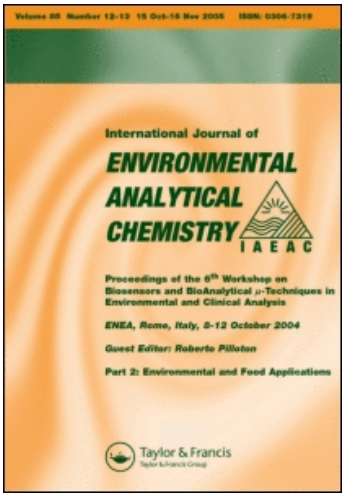

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Extraction and Recovery of Polychlorinated Dibenzodioxins and Dibenzofurans from Modified Method 5 Sampling Train Particulate Matter

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EXTRACTION AND RECOVERY OF POLYCHLORINATED DIBENZODIOXINS AND DIBENZOFURANS FROM MODIFIED METHOD 5 SAMPLING TRAIN PARTICULATE MATTER

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Because of the extreme toxicity of certain polychlorinated dibenzodioxin (PCDD) and dibenzofuran (PCDF) isomers, there is widespread concern regarding effective sampling and analysis for these compounds. One stationary source which raises concern is the effluent of hazardous waste incinerators where PCDDs/PCDFs may be formed during thermal destruction of hazardous waste. Particulate material in incinerator flue gas is collected on a quartz fiber filter in the sampling train recommended by the U.S. Environmental Protection Agency for collection of PCDDs and PCDFs. These halogenated organic compounds are recovered from the filter and from the sorbent of the sampling train by extraction with an organic solvent. To evaluate the effectiveness of this extraction process, a spiking study was performed using filters from various stationary sources. In comparing recoveries from particulate-laden filters to recoveries from spiked clean filters, no significant compound losses can be attributed to the particulate matter interactions in these samples. A modified sampling method has been written to address concerns about potential problems with recovery of PCDDs/PCDFs from particulate-laden sampling train filters.

KEY WORDS: Polychlorinated dibenzodioxins, polychlorinated dibenzofurans, hazardous waste incinerators, filters.

INTRODUCTION

In the United States, the response to the health concerns over the toxicity of PCDDs and PCDFs has been an effort to identify and reduce emissions of PCDDs and PCDFs into the environment. PCDDs and PCDFs, as well as other toxic, carcinogenic, and mutagenic organic compounds, have been detected in fly ash from municipal incinerators[1] and particulate effluent from other stationary sources. Incineration of refuse has been accepted for waste disposal since 1874[2]. In 1987, the U.S. Environmental

Protection Agency completed a survey of incinerator processes during which a database of emissions from 50 facilities was compiled[3]. PCDD and PCDF emissions were noted at all four types of incinerators, with a high variability in recorded concentrations due to the heavy dependence of the nature and concentration of emissions upon the composition of the waste stream and the temperature of combustion. The composition of the waste stream and the temperature of combustion are parameters which vary widely from site to site, and from day to day at a given site.

Particulate matter may comprise as much as 20% by weight of estimated total incinerator emissions[1]. Most modern incinerators have pollution control equipment including electrostatic precipitators for fly ash and other particulate matter. The fly ash consists of 70–95% inorganic matter, and PCDD/PCDF are among the organic compounds which have been reported as trace constituents of fly ash from hazardous waste incinerators[4–6]. Sampling and analytical methods for effluents from hazardous waste incinerators have been addressed by the U.S. Environmental Protection Agency using a Modified Method 5 (MM5) sampling train (Figure 1), with SW-846 Method 0010 as a guide to sampling methodology and SW-846 Method 8290 as an analytical methodology which incorporates the use of high resolution gas chromatography and high resolution mass spectrometry. EPA Method 23 includes both MM5 sampling and specific procedures for analysis of PCDD/PCDF in municipal solid waste incinerators and boilers and industrial furnaces. Sample preparation procedures in both of these methods include procedures for toluene extraction of MM5 train components using a Soxhlet extractor, with subsequent column chromatography procedures to remove potential analytical interferences from the extracts.

In current sample preparation procedures (Method 23 or Method 8290), the XAD-2® sorbent of the MM5 sampling train is spiked with a series of isotopically-labeled PCDD/PCDF standards prior to use in the field. In the laboratory, the resin is spiked with additional isotopically-labeled standards prior to extraction, and the resin and the particulate filter from the sampling train are extracted together. Analyte recoveries from this extraction procedure can vary widely because of the sample matrix and because of the sample preparation procedure which is used. The sorptivity of different fly ash samples for oganic compounds in general has been shown to vary widely[7]. Total carbon content of the fly ash has been shown to parallel sorptivity[8]. Analyses of some fly ash samples for organic compounds may be seriously biased unless there is a correction for extraction recoveries or sorptivity losses, with the losses becoming more pronounced as concentration levels decrease. PCDD and PCDF also show losses due to sorptivity[8].

The filter used in the Modified Method 5 sampling train is a glass- or quartz-fiber filter, without organic binder, exhibiting at least 99.95% efficiency (< 0.05% penetration) on 0.3-μm dioctyl phthalate smoke particles. The filter efficiency test is conducted by the manufacturer according to ASTM standard method D2986-71; the manufacturer supplies test data from his quality control program. Method 0010 does not specify a single source of supply. Any filters meeting the performance criteria may be used in the sampling trains. When the filter from the MM5 train, which usually contains fly ash particles after sampling at most stationary sources, is extracted together with the sorbent, there is no way to determine whether serious loss of analytes occurs due to sorptivity on the particulate material. To determine the severity of the problem with sorptivity of the particulate matter and to demonstrate a spiking procedure for the filters, filters which had been used in the field at five different stationary sources were spiked with a range of isotopically-labeled PCDD/PCDF standards and extracted to observe recoveries. In addition, a new draft sampling method, which requires separate analysis of the filter spiked with its own set of isotopically-labeled standards, has been written to ensure that extensive analyte losses from filters in the MM5 sampling train are recognized.

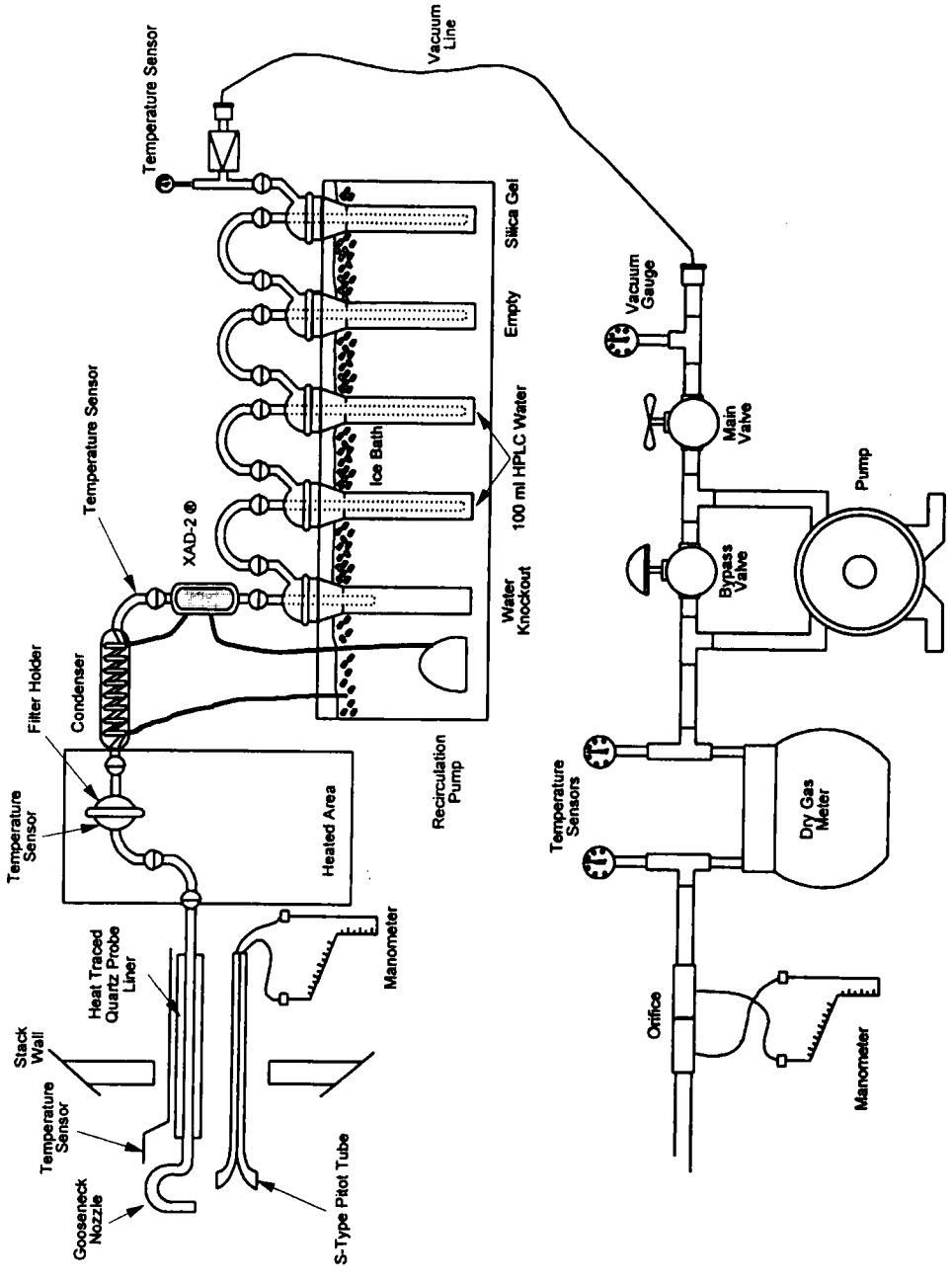

Figure 1 Schematic of CDD/CDF sampling train.

EXPERIMENTAL

Filters from MM5 sampling trains had been used in the field to sample at five different stationary sources. These filters were delivered to the laboratory in individual petri dishes. For each of the stationary sources, laboratory personnel selected three filters each, for a total of fifteen filters from five sources. Each filter was spiked with 4.0 ng of fifteen isotopically-labeled PCDD/PCDF standards shown in Table 1. Two pre-extracted filters were used as laboratory method blanks, and were spiked, extracted, and analyzed with the field filter samples. To ensure proper spiking, the isotopically-labeled PCDD/PCDF Standards solution (normally at a concentration of 0.1 ng/μL) was diluted to 0.004 ng/μL in isooctane, immediately before spiking the filters. Exactly 1.0 mL of this spiking solution was spiked uniformly onto the surface of each filter using an adjustable pipet. Each filter was transferred to a pre-extracted cellulose thimble in a Soxhlet extraction apparatus, with three 2 mL methanol rinses of the petri dish. The spiked filters were then subjected to 16 h Soxhlet extraction with toluene according to the procedures of EPA Method 23. Each extract was concentrated to 10 mL, spiked with 40 μL of a 0.1 ng/μL nonane solution containing the cleanup standard shown in Table 1, solvent-exchanged to hexane, then split 50:50. Half of each extract was archived, while the other half was subjected to column-chromatographic cleanup as described in EPA Method 23, and analyzed by high resolution gas chromatography/high resolution mass spectrometry, according to the procedures of EPA Method 23.

Table 1 Mean recoveries of spiked isotopically-labeled PCDD/PCDF standards.

Compound	*SIB Mean*	*% RSD*	*MWI Mean*	*% RSD*	*VD Mean*	*% RSD*	*CFPP Mean*	*% RSD*	*CK Mean*	*% RSD*	*Blanks Mean*
Cleanup Standard											
$^{13}Cl_4$-2,3,7,8-TCDD	54	15.2	58	30.5	41.7	8.4	60.9	29.9	57	11.9	47.8
Internal Standards											
$^{13}C_{12}$-2,3,7,8-TCDD	45.4	12.8	48.8	28.7	35.1	10.8	49.5	27.5	45.4	12.6	36.1
$^{13}C_{12}$-1,2,3,7,8-PeCDD	53.6	4.5	57.5	35	43	14.8	54.5	34.7	52.4	14.9	42.3
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	74.7	9.6	73	28.2	60.8	11.8	85	37.8	80.9	9.5	63.5
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	78	1.2	75.6	29.2	63.4	12	74.2	32.1	72	6.4	72.2
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	85.7	5.1	85.5	26.9	71.6	12.4	105	54.8	71.8	8.6	71.4
$^{13}C_{12}$-OCDD	83.2	11.4	86.8	29.5	75.5	12.2	86.5	57.3	56.8	14.8	65.2
$^{13}C_{12}$-2,3,7,8-TCDF	44	16.6	47.5	30.1	35.9	4.5	54.2	28.2	51.6	15.5	34.4
$^{13}C_{12}$-1,2,3,7,8-PeCDF	53.3	7.7	57.9	31.1	41.7	8.6	53.1	32.6	50.5	18.2	41.7
$^{13}C_{12}$-2,3,4,7,8-PeCDF	55.6	5.9	61.9	33.4	46.2	10.4	54.9	30.8	52.7	19.7	45.2
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	67.6	10.4	70.6	24.4	57.1	13.3	65.5	39.4	56.8	11.4	63
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	70.1	6	74.8	32.6	58.9	12.2	64.2	39.9	58	7.9	68.6
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	77.3	13.2	75.4	29.7	64.3	12.9	74.7	45	86	12	72.1
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	63.2	7.6	67.2	30.2	55.9	9.8	70.2	34.3	68.6	14.7	65.9
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	77.7	1.3	79.4	26.8	67.7	9.5	86.7	49.3	63.6	11.5	69.7
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	76.9	4	80.4	31.3	70.5	10.8	102.7	48.3	71	12.1	63.4

SIB = small industrial boiler burning chemical process wastes.
MWI = gas-fired starved air medical waste incinerator with carbon injection.
VD = ventilation duct in a nylon fiber spinning operation.
CFPP = coal-fired power plant.
CK = cement kiln burning hazardous wastes.

RESULTS AND DISCUSSION

The results of the extraction of the spiked filters are shown in Table 1. The filters had been used in sampling the following stationary sources with a MM5 sampling train:

SIB = small industrial boiler burning chemical process wastes;
MWI = gas-fired starved air medical waste incinerator with carbon injection;
VD = ventilation duct in a nylon fiber spinning operation;
CFP = coal-fired power plant; and
CK = cement kiln burning hazardous wastes.

These filters contained particulate matter deposited in the course of a one-hour sampling run. The set of filters used in the spiking study certainly does not encompass all possible stationary sources, but there is a reasonable representation and the medical waste incinerator (MWI), which includes carbon injection, should represent a worst case for the sorption of PCDD/PCDF on particulate matter. The carbonaceous material from the medical waste incinerator was distinctly visible on the filters prior to extraction. The best reproducibility was observed in the extraction of the small industrial boiler, the ventilation duct, and the cement kiln; the medical waste incinerator and the coal-fired power plant showed lower reproducibility, although still within the acceptable range. Recoveries of spiked analytes generally averaged 50% or better, with isolated exceptions. The major effect of the elevated carbon content of the particulate emissions appeared to be on the reproducibility of the analytical results: the highest relative standard deviations were observed at a coal-fired power plant, where elevated levels of carbonaceous particulate material would be expected. In this particular set of filters, losses of spiked material were not severe: no sets of recoveries < 10% were observed. However, this set of filters is only a small subset of available MM5 filters, some of which may very well show extensive losses of analyte recovery due to the sorptivity of the particulate material. To take a conservative approach to the recovery of PCDD/PCDF from the MM5 sampling train filters, a sampling/sample preparation methodology has been developed which requires separate spiking of the filters with isotopically-labeled PCDD/PCDF analogs with a separate preparation and analysis of the filters. Using this new procedure, a situation where MM5 filter particulate is so highly sorptive that quantitative recovery of PCDD/PCDF cannot be obtained will be recognized and appropriate action can be taken, whether this appropriate action consists of extensive correction of observed recovery or alternative sampling/preparation procedures.

Losses of spiked PCDD/PCDF were higher through the cleanup process than in the actual extraction process. EPA Method 23 incorporates a dual column cleanup, using a carbon column and a silica column. A triplicate set of filters was spiked and extracted, and the extract was dried, concentrated, and analyzed without the dual-column cleanup. The recoveries shown in Table 2 were obtained. The cleanup standard, $^{37}Cl_4$-2,3,7,8-TCDD, was added to the samples immediately before the column cleanup steps to evaluate compound losses in the column cleanup and concentration steps. The Internal Standards were spiked directly onto the particulate-laden filter to test the particulate matter, filter, and the extraction process. The cleanup process, incorporating two different column chromatography steps, appears to account for approximately 20% loss in recovery. Potentially interfering background constituents are minimized for an approximately 20% sacrifice in analyte recovery.

If approximately 20% of the analyte loss is due to the cleanup steps, then, on an analyte-by-analyte basis, 30–50% of the analyte is lost because it is not extracted from

Table 2 Recovery of PCDD/PCDF without cleanup.

Compound	*Percent Recovery*				
	B–25	*B–28*	*B–31*	*Mean*	*% RSD*
Cleanup Standard					
$^{13}Cl_4$-2,3,7,8-TCDD	75.6	62.9	79.1	72.5	11.8
Internal Standards					
$^{13}C_{12}$-2,3,7,8-TCDD	72.7	59.9	73.5	68.7	10.9
$^{13}C_{12}$-1,2,3,7,8-PeCDD	72.0	72.0	82.3	75.4	7.8
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	80.3	74.8	92.7	82.6	11.1
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	79.3	76.1	86.4	80.6	6.6
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	70.6	69.1	86.5	75.4	12.7
$^{13}C_{12}$-OCDD	56.2	51.3	69.6	59.0	16.0
$^{13}C_{12}$-2,3,7,8-TCDF	68.2	56.1	70.2	64.8	11.7
$^{13}C_{12}$-1,2,3,7,8-PeCDF	70.4	58.5	72.0	67.0	11.0
$^{13}C_{12}$-2,3,4,7,8-PeCDD	62.6	55.2	65.1	60.8	8.4
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	74.1	73.3	86.4	77.9	9.4
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	67.9	70.5	81.5	73.3	9.8
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	62.6	64.7	72.0	66.4	7.4
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	80.3	71.7	81.0	77.7	6.7
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	61.5	63.1	75.0	66.5	11.1
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	55.2	57.1	69.2	60.5	12.6

SIB = small industrial boiler burning chemical process wastes.
MWI = gas-fired starved air medical waste incinerator with carbon injection.
VD = ventilation duct in a nylon fiber spinning operation.
CFPP = coal-fired power plant.
CK = cement kiln burning hazardous wastes.

the particulate matter. In order to recognize that particulate retention of analyte can be a significant contributor to analyte loss, a sampling method for dioxin has been written to require separate preparation and analysis of the sorbent resin and the filter from the Modified Method 5 sampling train. If the filter and XAD-2® are prepared and analyzed separately, it is possible to use the same isotopically-labeled standards both for spiking the XAD-2® prior to its use in the field and for spiking the filter prior to its extraction. The same analytical procedure can be followed with both the filter and the resin, but two separate analyses must be performed. When the analyses are separated, extensive retention of PCDDs/PCDFs by the particulate material on the filter can be recognized if it occurs. The draft sampling/sample preparation method is under EPA review.

CONCLUSIONS

Because sorptive losses of PCDD/PCDF can occur due to the presence of particulate matter on the filter of the Modified Method 5 sampling train, separate analysis of the filter and the sorbent resin from this sampling train is recommended. When the filter and sorbent resin extraction is combined in the interests of economy, no additional isotopically-labeled standards are available to spike the filter separately, and extensive sorptive losses occurring because of the particulate matter on the filter will not be recognized, and the entire analysis can be compromised.

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