



Project Summary

Evaluation of an EPA High-Volume Air Sampler for Polychlorinated Dibenzo-*p*-Dioxins and Polychlorinated Dibenzofurans

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An EPA High-Volume air sampler was evaluated for retention and migration of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) within the sampler. This sampler, which is available from General Metal Works (GMW) as the Model PS-1 Sampler, consists of a filter, polyurethane foam adsorbent cartridge, air pump, and environmental housing. The use of an alternative adsorbent, silica gel, was also studied. Because of the high toxicity of selected PCDD/PCDF isomers and the limited availability of pure isomers, the study was carried out using 1,2,3,4-tetrachlorodibenzo-*p*-dioxin, 1,2,4,8-tetrachlorodibenzofuran, 1,2,3,4,7,8-hexachlorodibenzo-*p*-dioxin, 1,2,3,6,7,8-hexachlorodibenzofuran, octachlorodibenzo-*p*-dioxin, and octachlorodibenzofuran.

The sampler retained the isomers with approximately equal efficiencies when either PUF or silica gel was used as the adsorbent. The median retention efficiencies for the PCDD/PCDF isomers ranged from 67 to 124 percent when PUF was used, and from 47 to 133 percent when silica gel was used. In general, the lowest retention efficiencies were observed for the PCDF isomers and the highest retention efficiencies for the PCDDs. The overall average retention efficiency for all of the isomers at two concentration levels was 99 percent for both the PUF and the silica gel adsorbents.

Silica gel produced lower levels of background interferences than did PUF. The detection limits were therefore about four times lower for the tetrachlorinated isomers and 10 times lower for the hexachlorinated isomers when silica gel was used as the adsorbent. The difference in detection limit was approximately a factor of two for the octachlorinated isomers, which are of higher molecular weight than are the tetrachloro isomers, and consequently are less susceptible to interference. However, the silica gel was less convenient to work with and required more steps to clean up.

The desorption efficiency of the PCDD/PCDF isomers from spiked filters was evaluated to assess the extent of migration of these compounds from the filter to the adsorbent. Migration was dependent upon the isomers' chlorination level with the less chlorinated, more volatile isomers generally desorbing more efficiently. Tetrachlorinated isomers desorbed almost completely from the filter and were collected on the adsorbent, whereas the octachlorinated isomers were retained on the filters. Hexachlorinated isomers gave intermediate values of desorption from the filters.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully docu-

mented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are classes of tricyclic compounds that are extremely toxic and are of major environmental concern. Certain isomers, including 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF), have LD₅₀ values in the parts-per-trillion range for some animal species. Major sources of these compounds have been commercial processes involving polychlorinated phenols and polychlorinated biphenyls (PCB). Recently, however, combustion has been a source of PCDD and PCDF. A particularly significant source of these compounds is burning transformers and/or capacitors that contain PCBs and chlorobenzenes.

The objectives of this project were to determine the retention efficiency of the EPA High-Volume air sampler by measuring the retention and migration of selected PCDD and PCDF isomers within the sampler and to evaluate the utility of using silica gel as the adsorbent. Previous studies involving the collection of pesticides, PCBs, semivolatile industrial organic compounds, 1,2,3,4-TCDD and octachlorodibenzofuran (OCDF) have been successful. However, it was anticipated that silica gel would provide a lower background interference level and thus allow lower detection limits to be achieved.

The study consisted of spiking the filters or adsorbent cartridges of EPA High-Volume air samplers with selected PCDD/PCDF isomers. The PCDD/PCDF levels that remained on the filter or the adsorbent cartridge were then measured after a volume of approximately 325 m³ of air had been pulled through each sampler.

Procedure

Flow Rate Study

The air flow rates through various bed heights of silica gel were measured to determine if sufficient flow could be achieved. The silica gel was packed into glass cartridges and was held in place using a copper screen and thin layers of glass wool. The cartridge containing the silica gel was placed into a standard High-Volume sampler and flow was established. The experimental setup consisted of a High-Volume Sampler air

pump, a dry gas meter, an EPA gas flow calibrator, a filter holder, and a test cartridge containing the silica gel. The system was allowed to equilibrate for 30 minutes prior to recording the dry gas meter readings.

Retention Study

Known levels of PCDD/PCDF isomer were spiked into the sampler, and the levels of the PCDD/PCDF isomers remaining on the adsorbent cartridges and glass fiber filters following the sampling of approximately 325 m³ of clean air were measured. Two PCDD/PCDF levels, 150 ng and 5 ng of each isomer, were evaluated in triplicate. The PCDD/PCDF isomers were spiked into the sampler as n-decane solutions. For the experiment in which the spike was placed on the adsorbent cartridge, only the cartridge was analyzed. When the spike was placed on the filter, and filter and cartridge were analyzed separately. Two additional spiked cartridges, one each at the low and high levels, were also prepared for each adsorbent and held in the laboratory during the sampling sessions. Air was not pulled through these cartridges. These were used as reference samples to indicate if irreversible adsorption occurred as a function of time.

The test setup consisted of two high-volume sampler heads connected in series. The first sampler contained a microfiber glass filter and activated carbon to purify the air going into the second sampler, which contained the test filter and adsorbent cartridge.

Following the sampling, each of the cartridges and filters was spiked with 2,3,7,8-TCDD-¹³C₁₂ and octachlorodibenzo-p-dioxin-¹³C₁₂ (OCDD-¹³C₁₂) and Soxhlet-extracted with benzene for 18 hours. The high level samples, e.g., those spiked with 150 ng of the native isomers, were spiked with 50 ng of the labelled internal standards, while the low level samples were spiked with 5 ng of each internal standard. The benzene extracts were concentrated using a 3-stage Snyder column, diluted 1:1 with hexane, and cleaned up using acid/basetreated silica and alumina column chromatography. The final solutions were analyzed by high resolution gas chromatography/high resolution mass spectrometry. The spiking solutions were used to prepare response factor standards, thus eliminating the spiking solution concentration as a variable in the retention efficiency calculations.

Results

Flow Rate Study

Adequate flow air rates for sampling (Δ 150 std. L/min) were achieved for both meshes of silica gel and for all bed heights evaluated. Although the 6-12 mesh silica gel could be used with bed heights of up to 7.6 cm, the finer 35-70 mesh material was chosen to provide the greatest surface area for collection of the test PCDD/PCDF isomers. The results of the flow rate study are summarized in Table 1

Retention Study

The average retention efficiency for the PCDD/PCDF isomers spiked on filters was dependent upon the volatility of the particular isomer. In general, the tetrachlorinated isomers desorbed from the filters and were collected on the adsorbent, while the octachlorinated isomers remained on the filters. The hexachlorinated isomers exhibited intermediate behavior. When the data from the PUF and silica gel experiments are averaged at the two spiking levels, approximately 1.8 percent of the tetrachlorinated isomer spikes was retained on the filters, while 83 percent of the octachlorinated isomer spikes was retained after sampling. The hexachloro isomer spikes were retained on the filters at approximately 10 percent.

The average performance of the sampler for retention of PCDD/PCDF isomers is summarized in Tables 2 and 3. Table 2 summarizes the results for the sampler when PUF is used as the adsorbent and Table 3 the results when silica gel is used. All of the retention efficiencies are within ± 25 percent of quantitative, except for the two hexachloro isomers which vary by approximately ± 30 percent.

The adsorbent retention efficiencies for the HxCDD and HxCDF isomers were the lowest and the most variable of those measured. Although it is possible that these isomers were breaking through the adsorbents, it is also possible that they were lost during the sample workup. Since an isotopically labelled hexachlorinated dioxin or furan was not available for use as an internal standard, losses due to extraction and cleanup were corrected based on the recovery of the labelled tetrachlorinated standards. It was assumed that the volatility and extraction efficiency of these standards were similar to those of the hexachlorinated isomers, however, the validity of these assumptions has not been tested for all matrices.

Table 1. Flow Rates for Silica Gel Adsorbent

Experiment	Weight (g)	Mesh	Bed Height (cm)	Flow Rate (L/min)
1	30	35-70	2.5	190
2	60	35-70	4.5	160
3	30	6-12	1.9	230
4	60	6-12	3.2	220
5	90	6-12	5.1	220
6	120	6-12	6.4	215
7	150	6-12	7.6	215

Table 2. Retention Efficiency Performance of the PS-1 Sampler for PCDFs and PCDDs Using PUF as the Adsorbent

Medium	Spike Level, ¹ ng/m ³	Average Percent Recovery					
		TCDF	TCDD	HxCDF	HxCDD	OCDF	OCDD
Filter	0.5 ¹	0.3 ²	1.5	4.8	10	57	86
PUF		82	95	103	97	25	13
Total		82	96	108	107	82	99
Filter	0.02	2	0	1	3	26	41
PUF		79	95	93	104	71	67
Total		81	95	94	107	97	108

¹ Spike levels based on total weight of PCDD/PCDF isomer spiked, assuming 325 m³ of air were sampled.

² Average for three experiments

Table 3. Retention Efficiency Performance of the PS-1 Sampler for PCDFs and PCDDs Using Silica Gel as the Adsorbent

Medium	Spike Level, ng/m ³	Average Percent Recovery				
		TCDD	HxCDF	HxCDD	OCDF	OCDD
Filter	0.5	4.5	6.7	43	61	94
Silica Gel		74	62	92	21	2.5
Total		78	69	140	82	97
Filter	0.02	1.6	5.7	7.6	83	110
Silica Gel		74	63	83	8.1	6.8
Total		76	68	91	91	120

Conclusions and Recommendations

The retention efficiencies for the PCDD/PCDF isomers spiked into the samplers were in general quantitative agreement within experimental accuracy. The median retention efficiencies ranged from 67 to 124 percent when PUF was used as the adsorbent and from 47 to 133 percent when silica gel was used. The lowest retention efficiencies were observed for the PCDF isomers, particularly the tetrachlorinated and the hexachlorinated isomers.

Silica gel was found to be suitable as a replacement adsorbent for PUF. It can be packed into the same cartridge as the PUF and produces minimal resistance to the air flow. It does not degrade like PUF, and therefore produces lower levels of interfering compounds. Thus, the detection limits for the PCDD/PCDF were between two and ten times lower when silica gel was used as the adsorbent than when PUF was used.

When the PCDD/PCDF isomers were spiked onto the filter and approximately 325 m³ of clean air was drawn through

the samples, the isomers desorbed and were collected on the adsorbent. The degree of desorption was dependent upon the volatility of the isomer and tended to follow the level of chlorination. The tetrachlorinated isomers were almost completely desorbed from the filter, while the octachlorinated isomers showed only minimal migration. The hexachlorinated isomers desorbed at a degree intermediate to the tetrachlorinated and octachlorinated isomers.

The GMW PS-1 air sampler should be a suitable sampler for collection of PCDD/PCDF isomers from ambient air when either PUF or silica gel is used as the adsorbent. When PUF was used in these studies, the analytical detection limit was approximately 0.2 ng for TCDD and TCDF, which would compare to a theoretical ambient air detection limit of about 0.6 pg/m³ for a 24-hour sample. The use of chromatographic-grade silica gel improved detection limits by a factor of nearly four, to about 0.15 pg/m³. The silica gel, however, presented more difficulties in cleanup and use.

Due to the desorption of PCDD/PCDF isomers from the filter, the sampler will not provide samples that can be used to determine the particulate matter/vapor concentration distribution of the PCDD/PCDF isomers. If the lowest possible detection limits are needed, silica gel should be used as the adsorbent, since it is more stable than PUF and will, therefore, minimize interferences and provide the lowest possible detection limits.

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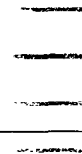
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