

Long-term and Conventional Sampling for PCDD/PCDF at Municipal and Hazardous Waste Incinerators Using Polyethylene as Adsorbent

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1. Introduction

In the eighties several sampling methods for PCDD/PCDF were tested for comparability and validity¹⁻⁷⁾. PCDD/PCDF emission concentrations during these tests were always above 1 ng TEQ/Nm³. These and other tests were used as a basis for the standardized methods of the VDI guidelines 3499⁸⁾. In Germany in 1990 the emission limit for PCDD/PCDF emission of waste incinerators was set to 0.1 ng I-TEQ/Nm³ in the 17.BImSchV, to be met for all incinerators by December 1, 1996. Other European countries have regulated the PCDD/PCDF emissions also to 0.1 ng I-TEQ/m³ or have set a guide value of 0.1 ng I-TEQ/m³ or have set a requirement to use the state of the art emission minimization techniques. Since no validated method for PCDD/PCDF measurements at incineration facilities at levels below 0.1 ng I-TEQ/m³ existed, the working group CEN/TC 264/WG 1 "Dioxins" started in 1992 to carry out comparative measurements and in 1994 validation measurements for PCDD/PCDF at these low levels. During these studies certain problems became evident^{9,10,11)}. One problem concerns sampling of stack gas downstream of adsorption systems using activated carbon. Another problem concerns the method of quantitation.

Results from the CEN comparative measurements⁹⁾ at a plant with an active coke-fixed bed adsorber may illustrate these points (Table 1). Using presampling spikes for quantitation results in emission values above 0.1 ng I-TEQ/m³. There were controversial discussions about the „correct“ method of quantitation in the CEN working group. In our opinion there is only one way to resolve this problem by developing a sampling procedure, which gives complete recovery of the presampling standards.

Table 1: Results obtained during comparative measurements by three different sampling methods, applied by six sampling teams.

Sampling Method	Dilution		Filter/Condenser		Cooled Probe		Mean
Sampling Institute	A	B	C	D	E	F	
Quantification with „Analytical Standards“	0,608*	0,113	0,069	0,073	0,095	0,060	0,082**
Quantification with „Presampling Standards“	0,888	0,149	0,275	0,282	0,149	0,082	0,187**

* Concentrations in ng I-TEQ/m³;

**Without value of sampling institute A

2. Materials and Methods

Principle of the sampling method. Stack gas is sucked under isokinetic conditions through an air cooled tube made of Titan and subsequently through an adsorbent filled cartridge made of V4A or Titan (5x12 cm). The temperature of the cartridge is kept at about 80 °C by a heated aluminum block. The gas stream enters the cartridge at the bottom. The content of the cartridge from bottom to top is as follows: a glass sintered filter plate to retain any dust particles and then the adsorbent. The adsorbent is filled into the cartridge in three sections, again from bottom to top. First 10% of the cartridge volume is plain adsorbent, then 50% adsorbent containing all 17 ¹³C-labeled 2,3,7,8-substituted PCDD/PCDF standards, and the remaining volume is filled again with plain adsorbent. To apply the standards 50 g of adsorbent are mixed with 250 ml of hexane and the standard mixture added. The solvent is removed under reduced pressure in a rotary evaporator under vacuum control.

Adsorbents used. In exhaustive preliminary experiments a number of organic and inorganic sorbents were tested under the aspect of a more or less quantitative recovery of applied standards both with and without actual sampling. Here only the results obtained with polyethylene as adsorbents are reported. The polyethylene used was obtained from BASF AG, Ludwigshafen, as a gift and has the commercial name „Lupolen UHM 301“. It is used as supplied without any previous cleaning.

Sampling volume. Depending on the sampling time 50 to 250 Nm³ were sampled resulting in a sampling volume of 2 to 0.3 m³/h.

PCDD/PCDF analysis: The adsorbent was removed from the cartridge together with the dust collected and extracted in a Soxhlet-apparatus with hexane for 20 h. The extract was divided in two equal parts. Part A was analyzed as such. To part B thalf the amount of ¹³C-labeled standard as before sampling was added. Clean-up of both parts was carried out by the modified, miniaturized procedure described previously ¹²⁾, using heat treatment with conc. sulfuric acid at 70°C and subsequent chromatography on a mini-column filled with Alumina B Super I for dioxin analysis (0.8 g, ICN Biomedicals). Analysis was carried out by either HRGC/HRMS (for short term sampling) or HRGC/LRMS (for long term sampling).

Calculation of presampling standard recovery. Native PCDD/PCDF content of each of the two parts of the extract was calculated on the basis of the standard amounts added. From the peak heights of native compounds and ¹³C-labeled standards in the two parts the recovery was calculated. For comparison the recovery was also calculated from native standard addition to part A.

3. Results and Discussion

Experiments with various adsorbents showed that even immediate extraction after application of standards as described above (addition of standards to adsorbent-solvent mixture and subsequent removal of solvent to dryness) did in most cases not result in a complete recovery of standards. With Polyethylene as adsorbent a complete recovery of standards was obtained under these conditions. That this is also the case in actual sampling experiments, carried out at the municipal waste incinerator at Stuttgart-Münster, Germany, which is equipped with a SCR-catalyst for NO_x and dioxin reduction, is shown in Table 2 for sampling periods of 2 to 7 days. The average standard recovery for individual sampling experiments ranged from 82 to 103 %, the overall recovery for the 7 sampling periods was 94 %. The variation in recoveries of individual standards is mainly due to the uncertainty of the analytical determination, which is also influenced by the ratio of peak heights of native compound to ¹³C-labeled standard.

During some of these sampling periods PCDD/PCDF sampling by the „cooled probe/absorption“ method was carried out by another sampling team (AMU, Donzdorf) for 6 h sampling periods. In Table 3 the results of three such partially parallel sampling periods are shown. The I-TEQ values per m³ are in good agreement, but they are of course not directly comparable due to the difference in sampling period. There are, however, differences between the two sampling methods which concern mainly the

Table 2: Recovery of presampling standards during long term sampling

Sampling time (days)	7	2	7	5	4	3	7	average
	recovery of presampling standards in %							recovery %
2,3,7,8-TetraCDD	102	112	93	105	86	97	85	97
1,2,3,7,8-PentaCDD	106	88	75	96	91	76	76	87
1,2,3,4,7,8-HexaCDD	100	123	91	102	108	76	86	98
1,2,3,6,7,8-HexaCDD	100	123	64	113	83	78	80	92
1,2,3,7,8,9-HexaCDD	100	177	95	74	100	88	91	104
1,2,3,4,6,7,8-HeptaCDD	91	57	126	96	105	101	82	94
OctaCDD	96	100	88	85	n.d.	n.d.	74	89
2,3,7,8-TetraCDF	95	99	90	73	83	91	76	87
1,2,3,7,8-PentaCDF	140	88	107	99	98	76	87	99
2,3,4,7,8-PentaCDF	82	88	75	86	75	88	71	81
1,2,3,4,7,8-HexaCDF	93	103	127	82	112	91	87	99
1,2,3,6,7,8-HexaCDF	93	103	159	118	101	80	93	107
1,2,3,7,8,9-HexaCDF	93	n.d.	n.d.	n.d.	62	74	76	76
2,3,4,6,7,8-HexaCDF	93	84	96	85	70	84	73	84
1,2,3,4,6,7,8-HeptaCDF	106	113	101	86	117	122	92	105
1,2,3,4,7,8,9-HeptaCDF	80	98	102	170	71	98	88	101
OctaCDF	117	84	116	91	n.d.	n.d.	82	98
Average recovery (%)	99	103	100	98	91	88	82	94

concentrations in total tetra- and pentaCDD/CDF. They are higher in the polyethylene adsorption method. This might be due to partial losses of lower chlorinated PCDD/PCDF in the cooled probe/absorption method. This has still to be clarified. There are also some differences in the concentrations of 2,3,7,8-substituted PCDD/PCDF, especially for octaCDD. This may in part be due to differences in absolute amounts analyzed. At least in one case correction for the average recovery of the two presampling standards used by AMU in the cooled probe/absorption method would have resulted in exceeding the 0.1 ng I-TEQ/m³ limit.

In Table 4 results from long term sampling over periods of more than 30 days are presented. Recoveries of presampling standards were again over 85% for the average standard recovery. In these sampling experiments more than 200 m³ were sampled during each sampling period. Therefore relatively large amounts of standard (25 to 50 ng for each congener) had to be added to the adsorbent. Average PCDD/PCDF emission concentrations during this long sampling periods were always below 0.05 ng I-TEQ/m³ and decreased within these 5 month, most likely due to operational changes. To our knowledge this is the first time that for an incinerator the uninterrupted average emission concentration for a five month period has been determined. The sampling at this incinerator is continued currently.

4. Conclusions

By using adsorbents that ensure a more or less complete recovery of presampling standards the question, how the quantitation should be carried out, becomes obsolete. All 17 ¹³C-labeled 2,3,7,8-substituted PCDD/PCDF standards are used as presampling standards and the native 2,3,7,8-substituted congeners, on which the I-TEQ calculation is based, are quantified directly on the basis of the presampling standards. Recovery determinations become only of scientific interest, but can be carried

out by standard addition of either native or ^{13}C -labeled standards as described. Both long and short term sampling can be carried out with an adsorbent like polyethylene. With this procedure the total annual emission of waste incinerators can be measured with reasonable cost. Whether this sampling procedure can also solve obvious sampling problems at incinerators with activated carbon sorbent systems will be investigated.

Table 3: Comparison of 6 h sampling using the „cooled probe/absorbent“ method with overlapping sampling periods using the polyethylene adsorption method

Sampling team	AMU	Uni Tbg.	AMU	Uni Tbg.	AMU	Uni Tbg.
date of sampling	12.10.95	4.-13.10.95	16.10.95	13.-17.10.95	20.10.95	17.-22.10.95
concentrations	ng/Nm ³	ng/Nm ³	ng/Nm ³	ng/Nm ³	ng/Nm ³	ng/Nm ³
TetraCDD	0,21	0,712	0,09	0,194	0,81	1,308
PentaCDD	0,38	0,619	0,17	0,184	1,14	0,664
HexaCDD	0,39	0,309	0,17	0,161	0,71	0,402
HeptaCDD	0,10	0,051	0,10	0,029	0,19	0,091
OctaCDD	0,20	0,056	0,36	0,045	0,32	0,081
TeraCDF	1,77	4,772	1,09	2,080	3,37	6,699
PentaCDF	1,02	3,225	0,64	0,803	2,48	3,227
HexaCDF	0,67	0,685	0,28	0,296	1,13	0,832
HeptaCDF	0,16	0,100	0,14	0,038	0,23	0,129
OctaCDF	0,04	0,010	0,03	0,006	0,03	0,012
2,3,7,8-TetraCDD	0,011	0,004	0,006	0,004	0,005	0,009
1,2,3,7,8-PentCDD	0,025	0,026	0,018	0,012	0,045	0,017
1,2,3,4,7,8-HexaCDD	0,017	0,009	0,010	0,003	0,025	0,013
1,2,3,6,7,8-HexaCDD	0,029	0,018	0,014	0,008	0,042	0,020
1,2,3,7,8,9-HexaCDD	0,017	0,007	0,014	0,003	0,025	0,007
1,2,3,4,6,7,8-HeptaCDD	0,051	0,029	0,062	0,014	0,081	0,036
2,3,7,8-TetraCDF	0,020	0,035	0,028	0,025	0,036	0,084
1,2,3,7,8-PentaCDF	0,067	0,071	0,036	0,046	0,205	0,174
2,3,4,7,8-PentaCDF	0,036	0,024	0,023	0,018	0,048	0,058
1,2,3,4,7,8-HexaCDF	0,073	0,052	0,030	0,021	0,069	0,076
1,2,3,6,7,8-HexaCDF	0,071	0,052	0,035	0,025	0,097	0,076
1,2,3,7,8,9-HexaCDF	0,004	0,002	0,002	0,002	0,005	0,003
2,3,4,6,7,8-HexaCDF	0,035	0,019	0,020	0,008	0,032	0,024
1,2,3,4,6,7,8-HeptaCDF	0,113	0,071	0,098	0,026	0,140	0,076
1,2,3,4,7,8,9-HeptaCDF	0,011	0,004	0,009	0,001	0,025	0,005
TCDD-Equiv. (I-TEQ)	0,073	0,053	0,046	0,031	0,098	0,087
<i>Recovery of sampling spikes</i>						
1,2,3,4-TetraCDD in %	79		96		74	
1,2,3,7,8,9-HexaCDD in %	76		85		73	
Average recovery	78		91		74	

Table 4: PCDD/PCDF emission concentrations after long term sampling at the municipal waste incinerator at Stuttgart-Münster, Germany.

sampling period	15.12.-23.1.	23.1.-15.2.	15.2.-11.3.	11.3.-29.3	29.3.-29.4
concentrations	ng/Nm3	ng/Nm3	ng/Nm3	ng/Nm3	ng/Nm3
TetraCDD	0,419	0,338	0,243	0,211	0,216
PentaCDD	0,259	0,261	0,158	0,225	0,185
HexaCDD	0,224	0,149	0,081	0,130	0,100
HeptaCDD	0,051	0,036	0,034	0,045	0,035
OctaCDD	0,074	0,086	0,067	0,020	0,050
Total PCDD	1,027	0,870	0,583	0,631	0,586
TetraCDF	2,550	1,740	1,506	1,800	2,130
PentaCDF	0,743	0,728	0,653	0,800	0,754
HexaCDF	0,248	0,302	0,214	0,307	0,149
HeptaCDF	0,071	0,047	0,028	0,042	0,050
OctaCDF	0,014	0,008	0,007	0,010	0,007
Total PCDF	3,626	2,825	2,408	2,959	3,090
2,3,7,8-TetraCDD	0,004	0,003	0,002	0,003	0,004
1,2,3,7,8-PentCDD	0,014	0,020	0,013	0,011	0,013
1,2,3,4,7,8-HexaCDD	0,014	0,005	0,001	0,002	0,002
1,2,3,6,7,8-HexaCDD	0,008	0,010	0,004	0,010	0,006
1,2,3,7,8,9-HexaCDD	0,004	0,005	0,004	0,008	0,005
1,2,3,4,6,7,8-HeptaCDD	0,028	0,020	0,015	0,020	0,017
2,3,7,8-TetraCDF	0,014	0,011	0,011	0,008	0,013
1,2,3,7,8-PentaCDF	0,033	0,035	0,044	0,032	0,040
2,3,4,7,8-PentaCDF	0,023	0,018	0,009	0,015	0,010
1,2,3,4,7,8-HexaCDF	0,021	0,028	0,016	0,028	0,012
1,2,3,6,7,8-HexaCDF	0,027	0,028	0,018	0,033	0,013
1,2,3,7,8,9-HexaCDF					
2,3,4,6,7,8-HexaCDF	0,012	0,017	0,005	0,010	0,004
1,2,3,4,6,7,8-HeptaCDF	0,043	0,036	0,018	0,028	0,036
1,2,3,4,7,8,9-HeptaCDF	0,004	0,001	0,002	0,002	0,001
TCDD-Equiv. (I-TEQ)	0,031	0,040	0,021	0,028	0,024

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