Contiuous Sampling of Dioxins and Furans in Flue Gas from Combustion Facilities

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1. Introduction

In the eighties four different sampling methods for PCDD/Fs in flue gas from combustion facilities had been developed and were tested.

The quasi-continuous PCDD/F sampling system presented here is based on the 'Adsorption Method' which was developed by GfA-company between 1988 and 1991. The aim of the project was to provide an easy-to-use method for sampling which results in fast sample clean-up and analysis, even at PCDD/F concentrations far below the limit of 0,1 ng ITE/m³ of the German 17. BImSchV.

The range of applications for the Adsorption Method in industrial and public R+D-projects and measurement programs includes raw gas, clean gas and process gases from many different plants, such as:

- municipal waste incinerators
- hazardous and industrial waste incinerators
- coal power plants
- lignine power plants
- sewage sludge incinerators
- wood combustion facilities
- pyrolysis plants
- soil decontamination plants
- shredder facilities
- aluminium melting facilities
- steel making plants
- cement kilns
- landfill gas engines

2. Principles of the Adsorption method

According to the VDI guideline 2066, part 1 and 3499, part 3, flue gas is succed under isocinetic conditions through a water-chilled suction tube with glass insert. Together with the usually ocurring condensate the gas is routed through an adsorption unit, consisting of a polymeric adsorbent which is connected downstream to a stuffed quartz wool filter which precipitates dust.
Normally only one glass cartridge filled with quartz wool and XAD-2 results from sampling as matrix to be analysed.

3. Continuous sampling system

Together with the automated sampling system AMESA the Adsoption Method is able to make a way of quasi-continuous monitoring of PCDD/Fs possible with only 12 PCDD/F analyses per year.

In the system flue gas is cooled rapidly in a water-cooled probe made of titanum to assure optimum and reproducible adsorption of flue gas components. The PCDD/Fs are deposited in the collection unit witch is a combination of quartz wool and an organic polymer (pretreated XAD-2). PCDD/Fs present in the condensate are completely adsorbed as well.

After deposition of the PCDD/Fs, the flue gas is cooled down to 5°C to completely remove water. The condensate is discontinuously pumped out of the system and is used to check the sampled gas volume.

The dry measuring gas volume flow is measured. The process control unit assures isokinetic sampling depending on flue gas velocity, temperature and pressure in the flue gas ducts. A simple and straightforward software assures easy handling of the sampling equipment and also provides the option of adding user-defined data into the sampling protocol. All registered and calculated data as well as the sampling protocol are stored on a hard disc.

3. Sampling periods

Today the VDI guideline 2066, Part 1 and 3499, part 3 requires a 2 to 16 h sampling period for Dioxins/Furans. To improof the Adsoption method's suitability in comparison to conventional methods it was necessary to do a lot of measurement work. This is to introduce the results from part of these measurements.

3.1 Short-term sampling (2 to 16 h sampling periods)

To determine relative standard deviations of the complete method (sampling and analysis) 8 parallel samplings were performed in the flue gas of a combustion facility with relatively

high PCDD/F concentrations (approx. 0,2 ng ITE/m³) and 5 parallel samplings were executed at relatively low PCDD/F concentrations (approx. 0,02 ng ITE/m³) using two trains accordings to the Adsorption Method. The following table will give an example.

Parameter	x	s	s_{rel}	n
PCDF/PCDDs	ng/m³	ng/m³	%	
Total TetraCDFs	40.7	3.6	9	8
Total PentaCDFs	27.0	3.3	12	8
Total HexaCDFs	12.1	1.1	9	8
Total HeptaCDFs	4.0	0.5	13	8
OctaCDF	0.6	0.3	50	5
Total Tetra- to OctaCDFs	84.4	7.1	8	8
2378-TetraCDF	1.54	0.17	11	8
12378-/12348-PentaCDF[a]	2.63	0.30	11	8
23478-PentaCDF	1.32	0.19	14	8
123478-/123479-HexaCDF[a]	1.71	0.17	10	8
123678-HexaCDF	1.74	0.18	10	8
123789-HexaCDF	0.16	0.04	25	8
234678-HexaCDF	0.71	0.06	8	8
1234678-HeptaCDF	3.04	0.38	13	8
1234789-HeptaCDF	0.21	0.06	29	8
Total TetraCDDs	3.6	0.4	11	8
Total PentaCDDs	3.9	0.6	15	8
Total HexaCDDs	3.1	0.5	16	8
Total HeptaCDDs	2.4	0.3	13	8
OctaCDD	3.0	0.4	13	8
Total Tetra- to OctaCDDs	16.1	1.6	10	8
2378-TetraCDD	0.28	0.03	11	8
12378-PentaCDD	0.62	0.06	10	8
123478-HexaCDD	0.21	0.04	19	8
123678-HexaCDD	0.28	0.03	11	8
123789-HexaCDD	0.40	0.03	8	8
1234678-HeptaCDD	1.26	0.12	10	8
Total Tetra- to OctaCDF/Ds	100.4	8.5	8	8
ITE (NATO/CCMS 1988) excl. LOD	2.11	0.22	10	8

Totals include detected congeners only; LOD = limit of detection
a not separable on SP 2331 GC stationary phase

3.2 Long-term sampling (6 hrs up to 4 weeks sampling periods)

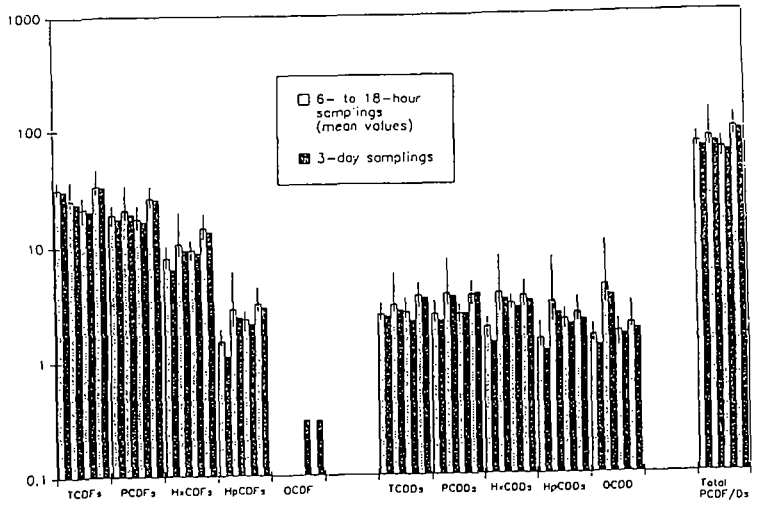
In the scope of 2 measuring campaigns with sampling periods of 3 to 5-days and 1 to 4-week the distribution of PCDD/Fs in the sampling equipment for longer sampling periods was examined. Potential break-through was checked in the scope of five 1 to 4-week samplings by back-up XAD-2 cartridge connected downstream of the adsorption unit. There are no differences between the break-throughs for the one-week samples and for the four-week sample which will be shown in the following table.

Sampling Period	4 weeks	1st week	2nd week	3rd week	4th week
Sample	S 1	S 2	S 3	S 4	S 5
PCDF/PCDD	ng/m³	ng/m³	ng/m³	ng/m³	ng/m³
Total TetraCDFs	66,6	51,4	61,4	50,2	52,7
Total PentaCDFs	58,4	44,5	47,4	41,6	46,8
Total HexaCDFs	27,6	20,3	21,4	20,5	21,9
Total HeptaCDFs	7,2	5,9	6,1	6,1	6,9
OctaCDF	< 0,2	< 0,2	< 0,2	0,6	< 0,3
Total Tetra- to OctaCDFs	158,8	122,1	136,3	119,0	128,3
2378-TetraCDF	2,54	2,83	3,40	2,60	2,79
12378-/12348-PentaCDF[a]	5,49	4,67	5,06	4,21	5,07
23478-PentaCDF	3,12	2,59	2,95	2,55	2,75
123478-/123479-HexaCDF[a]	3,73	2,93	3,19	2,97	3,39
123678-HexaCDF	3,80	3,16	3,34	3,07	3,58
123789-HexaCDF	0,42	0,25	0,29	0,27	0,32
234678-HexaCDF	1,57	1,39	1,40	1,28	1,27
1234678-HeptaCDF	5,54	4,71	4,71	4,54	5,30
1234789-HeptaCDF	0,28	< 0,20	0,25	0,28	0,25
Total TetraCDDs	7,3	5,8	6,9	5,6	6,1
Total PentaCDDs	8,1	6,2	7,0	6,3	6,7
Total HexaCDDs	6,4	5,3	5,7	5,1	5,3
Total HeptaCDDs	5,3	4,9	5,8	4,2	4,4
OctaCDD	3,6	3,8	4,2	2,7	2,1
Total Tetra- to OctaCDDs	30,7	26,0	29,6	23,9	24,6
2378-TetraCDD	0,63	0,52	0,60	0,52	0,56
12378-PentaCDD	1,49	0,99	1,06	1,01	1,15
123478-HexaCDD	0,48	0,37	0,40	0,38	0,41
123678-HexaCDD	0,60	0,50	0,55	0,48	0,49
123789-HexaCDD	0,64	0,56	0,57	0,57	0,60
1234678-HeptaCDD	2,82	2,67	3,15	2,26	2,33
Total Tetra- to OctaCDF/Ds	189,5	148,1	165,9	142,9	152,9
ITE (NATO/CCMS 1988) excl. LOD	4,68	3,82	4,26	3,75	4,13

Totals include detected congeners only; LOD = limit of detection
a not separable on SP-2331 GC stationary phase

4. Results

To prove comparability of PCDD/F results from 6 to 16-hour sampling to those from samplings lasting more than 16 hours, 23 18-h samplings were performed parallel to 4 three-day samplings. In a second measuring campaign at the same incinerator 4 weekly samplings were performed parallel to one 4-week sampling.



According to these results the Adsorption method prooved to be appropiate for the determination of PCDD/Fs in flue gas e.g. from combustion facilities even in short-term and long-term samplings. Comprehensive performance characteristics according to the the requirements of the VDI guideline series 3499 for relatively high PCDD/F concentrations (> 1ng ITE/m³) and for relatively low PCDD/F concentrations (< 0,1ng ITE/m³) are published. This assures the verification of the threshold value of 0,1 ng ITE/m³ in accordance with the 17. BImSchV. The Adsorption method is suitable for PCDD/Fs measurement over 6h up to 4-week periods.

5. References

1) W. Funcke, H. Linnemann : ' Measuring of polychlorinated dibenzofurans (PCDFs), dibenzo(p)dioxins (PCDDs) and further organic compounds of similar volatility and polarity in flue gas of combustion facilities using the 'Adsorption Method' ', Münster-Roxel, 1995

2) GfA, bm becker meßtechnik : ' AMESA - Comprehensive Method for continuous sampling of dioxins and furans in flue gas from combustion facilities ', 1995