VALIDATION OF A STACK SAMPLING METHOD ACCORDING TO EN 1948 FOR PCDD/F AND OTHER SEMI-VOLATILE ORGANIC COMPOUNDS

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Introduction

Stack sampling for dioxins and furans (PCDD/F) according to the European Standard EN 1948[1] may be carried out by one of three different methods: the filter/condenser method, the dilution method and the cooled probe method. For each method a validation of the applied sampling train is required. This validation has to show that a possible breakthrough of dioxins and furans after the last stage of the sampling train is less than 10 % related to the total amount of PCDD/Fs sampled. Normally with a state of the art sampling train there is no worth mentioning breakthrough to be expected and most of the laboratories that carry out stack sampling may have provided their method validation for PCDD/Fs. However EN 1948 is frequently used not only for PCDD/F measurements but also for determination of other semi-volatile organic compounds in stack gases such as polychlorinated biphenyls (PCB), polychlorinated benzenes (PCBz), polychlorinated phenols (PCPh), polychlorinated naphthalenes (PCN) and polycyclic aromatic hydrocarbons (PAH). For this partly higher volatile compounds we see a considerable lack of validation data.

In this paper an example for application of the cooled probe method is described which is easily to be handled representing a state of the art sampling train after 5 years experience with EN 1948. For the validation we performed samplings in the stack gas of an iron ore sintering plant, knowing that PCB, PCBz, PCPh, PCN and PAH are present in well detectable concentrations. The last adsorption stage consisting of an XAD-2 cartridge was carried out twice and breakthrough of the corresponding compounds from the first to the second XAD-2 cartridge was determined.

Materials and Methods

A sampling train according to the cooled probe method of EN 1948-1 was used. A sketch of the original sampling train (without double adsorption stage) is shown in Figure 1 and consequently the sampling train fulfils all mandatory requirements of the standard. In contrast to the examples given in the informative part of EN 1948-1 we usually use only one solid absorption stage which is an XAD cartridge filled with 30 g of pre-cleaned XAD-2 resin. Only for validation measurements the XAD cartridge was doubled.

Samplings were conducted according to EN 1948 considering the requirements of VDI guideline 2066, part 1, for isokinetic sampling. Two samples were taken from the stack gas of an iron ore sintering plant after the electric precipitator (ESP). Flue gas conditions and sampling parameters are summarized in Table 1.

After sampling the original sampling train with the first XAD cartridge and the back-up cartridge were extracted separately with toluene in a soxhlet extractor (solids) and by liquid-liquid extraction in a separation funnel (condensate) respectively. The combined extracts were divided into four parts. The clean up was performed separately for PCDD/F, PCB/PCBz/PCN, PCPh and PAH by individual

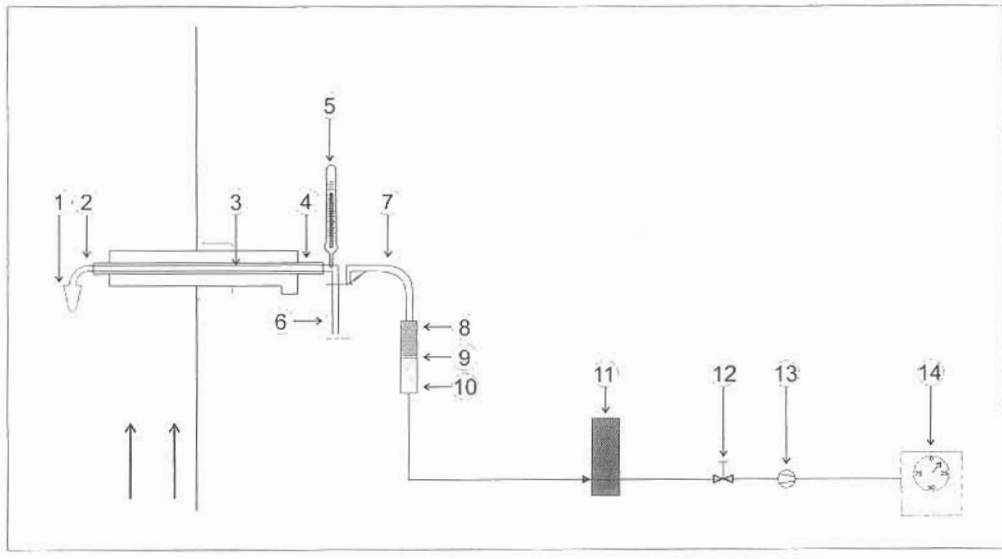

Figure 1. Sampling train according to EN 1948-1, cooled probe method, (GfA type).

1 Nozzle	6 Condensate flask	11 Drying agent (silica)
2 Elbow joint	7 Glass joint	12 Valve
3 Inside glass tube	8 Quartz wool	13 Suction device
4 Cooled probe	9 Filter (S&S, GF10HY)	14 Dry gas meter
5 Thermocouple	10 Solid adsorber (XAD-2)	

Table 1. Flue gas conditions and sampling parameters during validation measurements.

Flue gas temperature	160 – 170 °C	Sampling time	6 hours
Flue gas moisture	50 – 60 g/Nm^3	Sample volume	5.5 – 6.0 Nm^3
Flue gas velocity	15 m/s	Temperature after cooler	20 – 22 °C
Dust concentration	35 mg/Nm^3	Pressure in sampling train	80 – 90 kPa

adsorption chromatography. For analysis of PCDD/Fs we used a HRGC/HRMS system (HP 5890A/VG AutoSpec), all other compounds were analyzed with a HRGC/LRMS system (Agilent 6890/Agilent 5973). PCPhs were acetylated with acetic anhydride prior to analysis.

Results and Discussion

The results of the validation measurements are shown in the following Tables 2 to 5. This data show that detected amounts in the back-up cartridge are in the range of 0.02 to 3.07 % (bold numbers) but most of the components could not even be detected in the back-up cartridge. In this case a maximum value for breakthrough is given in brackets.

Detectable concentrations in the back-up cartridge could only be found for PCDD/Fs and PAHs and all values are significantly below 10 % of the amount in the original sampling train. Moreover this detected concentrations in the back-up cartridge are altogether in the range of blank values so we conclude that there is no real breakthrough even for these compounds. Although many compounds

were not detected in the back-up cartridge we can derive from the detection limits that possible breakthroughs of PCDD/F, PCPh and PAH are below 10 % and are therefore within the requirements of EN 1948. For PCB, PCPh and PCN the ratio between detected concentrations and detection limits was to small to prove without gap a breakthrough below 10 %.

References

1. European Standard: CEN/EN 1948, September 1996, Stationary source emissions – Determination of the mass concentration of PCDD/PCDFs, Part 1 - 3

Table 2.

PCDD/F	Original sampling train		Back-up cartridge		"Breakthrough"	
Dimension	Sample 1 ng/Nm³	Sample 2 ng/Nm³	Sample 1 ng/Nm³	Sample 2 ng/Nm³	Sample 1 %	Sample 2 %
2,3,7,8-TetraCDF	0.315	0.326	< 0.00026	0.00050	(< 0.08)	**0.15**
1,2,3,7,8-PentaCDF[a]	0.348	0.427	< 0.00038	0.00053	(< 0.11)	**0.12**
2,3,4,7,8-PentaCDF	0.527	0.567	< 0.00042	0.00055	(< 0.08)	**0.10**
1,2,3,4,7,8-HexaCDF[a]	0.427	0.452	< 0.00041	0.00048	(< 0.10)	**0.11**
1,2,3,6,7,8-HexaCDF	0.336	0.346	< 0.00036	0.00047	(< 0.11)	**0.14**
1,2,3,7,8,9-HexaCDF	0.003	0.133	< 0.00020	< 0.00006	(< 6.67)	(< 0.05)
2,3,4,6,7,8-HexaCDF	0.332	0.355	0.00042	0.00045	**0.13**	**0.13**
1,2,3,4,6,7,8-HeptaCDF	0.567	0.653	0.00095	0.00116	**0.17**	**0.18**
1,2,3,4,7,8,9-HeptaCDF	0.013	0.128	< 0.00020	< 0.00014	(< 1.54)	(< 0.11)
1,2,3,4,6,7,8,9-OctaCDF	0.230	0.240	0.00090	0.00120	**0.39**	**0.50**
2,3,7,8-TetraCDD	0.007	0.008	< 0.00020	< 0.00010	(< 2.86)	(< 1.25)
1,2,3,7,8-PentaCDD	0.031	0.032	< 0.00024	< 0.00013	(< 0.77)	(< 0.41)
1,2,3,4,7,8-HexaCDD	0.026	0.027	< 0.00032	< 0.00008	(< 1.23)	(< 0.30)
1,2,3,6,7,8-HexaCDD	0.039	0.041	< 0.00027	< 0.00007	(< 0.69)	(< 0.17)
1,2,3,7,8,9-HexaCDD	0.031	0.037	< 0.00027	< 0.00007	(< 0.87)	(< 0.19)
1,2,3,4,6,7,8-HeptaCDD	0.163	0.171	0.00184	0.00091	**1.13**	**0.53**
1,2,3,4,6,7,8,9-OctaCDD	0.150	0.150	0.00460	0.00330	**3.07**	**2.20**
I-TEQ	0.463	0.510	0.00008	0.00052	**0.02**	**0.10**

a co-elution with 1,2,3,4,8-PentaCDF and 1,2,3,4,7,9-HexaCDF on GC column SP-2331 is possible

Table 3.

PCB, PCBz, PCPh	Original sampling train		Back-up cartridge		"Breakthrough"	
Dimension	Sample 1 µg/Nm³	Sample 2 µg/Nm³	Sample 1 µg/Nm³	Sample 2 µg/Nm³	Sample 1 %	Sample 2 %
PCB 28	0.002	0.003	< 0.001	< 0.001	(< 50)	(< 33)
PCB 52	0.004	0.005	< 0.001	< 0.001	(< 25)	(< 20)
PCB 101	0.003	0.004	< 0.001	< 0.001	(< 33)	(< 25)
PCB 153	0.002	0.003	< 0.001	< 0.001	(< 50)	(< 33)
PCB 138	0.002	0.002	< 0.001	< 0.001	(< 50)	(< 50)
PCB 180	0.001	0.001	< 0.001	< 0.001	(< 100)	(< 100)
1,3,5-TriCBz	0.240	0.399	< 0.004	< 0.004	(< 1.7)	(< 1.0)
1,2,4-TriCBz	2.137	2.174	< 0.004	< 0.004	(< 0.2)	(< 0.2)

PCDD/F SURROGATES

1,2,3-TriCBz	1.342	0.948	< 0.004	< 0.004	(< 0.3)	(< 0.4)
1,2,3,5/1,2,4,5-TetraCBz	1.132	1.176	< 0.004	< 0.004	(< 0.4)	(< 0.3)
1,2,3,4-TetraCBz	0.802	0.701	< 0.004	< 0.004	(< 0.5)	(< 0.6)
1,2,3,4,5-PentaCBz	0.542	0.623	< 0.004	< 0.004	(< 0.7)	(< 0.6)
1,2,3,4,5,6-HexaCBz	0.085	0.099	< 0.004	< 0.004	(< 4.7)	(< 4.0)
2,4,6-Trichlorphenol	1.465	1.529	< 0.007	< 0.007	(< 1)	(< 1)
2,3,6-Trichlorphenol	0.050	0.059	< 0.007	< 0.007	(< 14)	(< 12)
2,3,5-Trichlorphenol	0.047	0.052	< 0.007	< 0.007	(< 15)	(< 14)
2,4,5-Trichlorphenol	0.079	0.084	< 0.007	< 0.007	(< 9)	(< 8)
2,3,4-Trichlorphenol	0.069	0.074	< 0.007	< 0.007	(< 10)	(< 10)
3,4,5-Trichlorphenol	0.007	0.008	< 0.007	< 0.007	(< 100)	(< 88)
2,3,5,6-Tetrachlorphenol	0.010	0.014	< 0.007	< 0.007	(< 70)	(< 50)
2,3,4,6-Tetrachlorphenol	0.235	0.277	< 0.007	< 0.007	(< 3)	(< 3)
2,3,4,5-Tetrachlorphenol	0.029	0.032	< 0.007	< 0.007	(< 24)	(< 22)
2,3,4,5,6-Pentachlorphenol	0.060	0.059	< 0.007	< 0.007	(< 12)	(< 12)

Table 4.

PAH, PCN	Original sampling train		Back-up cartridge		"Breakthrough"	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
Dimension	µg/Nm³	µg/Nm³	µg/Nm³	µg/Nm³	%	%
Naphthalene	35.85	38.68	0.70	0.18	**2.0**	**0.5**
Acenaphthylene	2.61	2.88	< 0.02	< 0.01	(< 0.8)	(< 0.3)
Acenaphthene	1.80	1.99	< 0.02	< 0.01	(< 1.1)	(< 0.5)
Fluorene	2.23	2.44	< 0.02	< 0.01	(< 0.9)	(< 0.4)
Phenanthrene	7.78	9.07	< 0.03	< 0.02	(< 0.4)	(< 0.2)
Anthracene	0.63	0.72	< 0.01	< 0.01	(< 1.6)	(< 1.4)
Fluoranthene	2.54	2.88	< 0.01	< 0.01	(< 0.4)	(< 0.3)
Pyrene	1.19	1.36	< 0.01	< 0.01	(< 0.8)	(< 0.7)
Benz(a)anthracene	0.64	0.70	< 0.01	< 0.01	(< 1.6)	(< 1.4)
Chrysene	0.92	1.01	< 0.01	< 0.01	(< 1.1)	(< 1.0)
Benzo(b/j)fluoranthene[a]	1.41	1.66	< 0.01	< 0.01	(< 0.7)	(< 0.6)
Benzo(k/j)fluoranthene[a]	0.58	0.55	< 0.01	< 0.01	(< 1.7)	(< 1.8)
Benzo(a)pyrene	0.58	0.67	< 0.01	< 0.01	(< 1.7)	(< 1.5)
Dibenz(a,h)anthracene	0.33	0.36	< 0.01	< 0.01	(< 3.0)	(< 2.8)
Benzo(ghi)perylene	0.62	0.69	< 0.01	< 0.01	(< 1.6)	(< 1.4)
Indeno(1,2,3-cd)pyrene	0.84	0.98	< 0.01	< 0.01	(< 1.2)	(< 1.0)
2-MonoCN	0.181	0.242	< 0.004	< 0.004	(< 2.2)	(< 1.7)
1-MonoCN	0.149	0.204	< 0.004	< 0.004	(< 2.7)	(< 2.0)
1,4-DiCN	0.010	0.012	< 0.004	< 0.004	(< 40.0)	(< 33.3)
1,5-DiCN	0.022	0.027	< 0.004	< 0.004	(< 18.2)	(< 14.8)
2,7-DiCN	0.037	0.041	< 0.004	< 0.004	(< 10.8)	(< 9.8)
1,2-DiCN	0.046	0.053	< 0.004	< 0.004	(< 8.7)	(< 7.5)
2,3-DiCN	0.028	0.035	< 0.004	< 0.004	(< 14.3)	(< 11.4)
1,8-DiCN	< 0.004	< 0.004	< 0.004	< 0.004	b	b
1,2,7-TriCN	< 0.004	< 0.004	< 0.004	< 0.004	b	b
1,2,3,4-TetraCN	< 0.004	< 0.004	< 0.004	< 0.004	b	b
1,2,3,6,7-PentaCN	< 0.004	< 0.004	< 0.004	< 0.004	b	b
1,2,3,4,6,7-HexaCN	< 0.004	< 0.004	< 0.004	< 0.004	b	b
1,2,3,4,5,6,7-HeptaCN	< 0.004	< 0.004	< 0.004	< 0.004	b	b
OctaCN	< 0.004	0.008	< 0.004	< 0.004	b	(< 50.0)

a not separated on GC column DB-5;b compound not detected in flue gas