VALIDATION OF A LONG TERM SAMPLING SYSTEM FOR PCDD/F

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Abstract
There is still a discrepancy between emission and immission inventories for PCDD/F [1]. Emission inventories are usually based on few 8 hour emission samples. With this short term samples a real mass balance of what a plant is emitting is only roughly estimable. Depending on the actual operating condition big differences of the level of pollutants in emission are possible. Long term sampling systems for PCDD/F can be used to cover long periods, so a more realistic emission balance can be obtained. Evaluation of the accuracy of long term sampling systems should be done in order to assure the quality of the generated data.

Introduction
The reference methods for sampling and analysis of PCDD/F in emission of stationary emission sources are EN 1948 and US EP 23 [2]. Both methods are based on manual sampling systems and usually relate to 6 to 8 hours sampling time. But a sampling time of 8 hours covers only a marginal period of the yearly operation of an average industrial plant. Especially in the case of industrial plants using not homogeneous combustibles like household waste or RDF (Refused Derived Fuel) emissions levels of certain pollutants can be strongly linked to the actual combustion conditions. Thus a 8 hour PCDD/F emission sample resembles more the technical ability of the flue gas cleaning systems of a plant to fulfil the respect of emission limits then the real emission level. To close the gap between emission and immission inventories it is very helpful to sample emissions of plants using a long term sampling, system covering nearly all the operation time of a plant.
Utilizing a long term sampling system for PCCD/F emission analysis, enables to sample for two weeks and more. So different combustion conditions you can have also on several days in a plant are still covered by this sampling technique. Long term systems are more and more installed and therefore we should focus on accuracy of the measurement results we get. The only way is to compare the results of long term sampling systems with manual reference (short term) sampling on a 6 to 8 hour basis [3].
By a simple parallel measurement of a long term sampling system against a manual standard reference sampling system we can evaluate if the system is working properly during the 6 to 8 hours normally used in manual sampling. Attempting to measure with the manual standard reference method EN 1948 for more than 8 hours brings the system to sample at conditions for which the methods is not validated [2].
By sampling more than 24 hours with a manual system the risk is to go beyond the limits of what is possible. For example with cooled probe and filter cooler method the collected condense water after on day is normally to much for the standard collecting vessels.

Materials and methods
The emission samples where taken at a incineration plant for biomass (waste wood) that utilize up to 15% of RDF (Refused Derived Fuel). Three incineration lines with an overall capacity of approximately 100,000 tons per year are based on the same technical build-up. The combustion takes place on a fluidized bed. The flue gas cleaning system consists of a cyclone filter, a acid wet scrubber, a wet electrostatic filter and finally a basic wet scrubber with addition of activated carbon slurry. The temperature (37°C) and the humidity (5 % (v/v) were practical identical on the two stacks. The dust concentration was different. On stack 1 (relates to incineration line 1) we had about 5 mg/Nm3, whereas on stack 2 (relates to incineration line 2 and 3) less than 1 mg/Nm3 was measured.
PCCD/Fs sampling, clean up and quantification were conducted in accordance with actual European Standard Protocols EN 1948/2006 [2]. Manual flue gas sampling was performed by the filter-cooler method and conducted with automatic, continuous adjusting isokinetical sampling systems (Zambelli). An automatic sample prep system (Dioxin Prep, Fluid Management System Inc.) was used for chromatographic clean up. Quantification of PCDD/F was done by HRGC-HRMS (Thermofinnigan MAT 95XP).

To evaluate the performance of the automatic long term system parallel measurements were performed with manual (reference)sampling systems. To evaluate also the variability between the standard reference methods two manual sampling systems were used. Parallel sampling, using two manual reference systems (Zambelli, filter condenser) M1 and M2 were performed contemporaneous to the long term system (AMESA) based on the cooled probe method [4]. So three parallel measurements lasting 8 hours, two manual reference sampling, one long term sampling, were performed to evaluate the accuracy of the long term system.
In addition a 24 hour parallel measurement was done by using a manual reference system (M) and the long term system (AMESA).
The sampling probe tubes were installed in a way to have the sampling nozzles as close as possible.
The manual system used a 6 mm diameter nozzle, the long term system a 5 mm nozzle. At the end of sampling approximately 6 Nm^3 were sample with the long term system and approx. 8 Nm^3 with the manual system.

Results and Discussion

Table 1: PCDD/F results for all samplings: all results in ng /Nm^3 (dry gas referd to 11% O2)

	Stack 1					Stack 2				
	8 h sampling			24 h sampling		8 h sampling			24 h sampling	
	M1	M2	AMESA	M	AMESA	M1	M2	AMESA	M	AMESA
2378 TCDD	0.0012	0.0010	0.0010	0.0009	0.0006	0.0003	0.0004	0.0002	0.0006	0.0003
12378 PCDD	0.0016	0.0021	0.0023	0.0018	0.0011	0.0005	< 0.0005	< 0.0005	0.0006	< 0.0005
123478 HxCDD	< 0.0010	< 0.0010	< 0.0010	0.0011	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
123678 HxCDD	0.0018	0.0020	0.0010	0.0023	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
123789 HxCDD	< 0.0010	< 0.0010	< 0.0010	0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
1234678 HpCDD	0.0028	0.0037	0.0031	0.0056	0.0015	0.0021	0.0016	< 0.0010	< 0.0010	< 0.0010
OCDD	< 0.0050	< 0.0050	0.0085	0.0057	< 0.0050	0.0056	< 0.0050	< 0.0050	< 0.0050	< 0.0050
2378 TCDF	0.0132	0.0140	0.0118	0.0100	0.0181	0.0038	0.0029	0.0043	0.0052	0.0038
12378 PCDF	0.0176	0.0223	0.0206	0.0209	0.0120	0.0067	0.0059	0.0032	0.0058	0.0040
23478 PCDF	0.0201	0.0278	0.0235	0.0267	0.0181	0.0059	0.0040	0.0059	0.0056	0.0032
123478 HxCDF	0.0141	0.0178	0.0155	0.0179	0.0084	0.0037	0.0050	0.0027	0.0032	0.0022
123678 HxCDF	0.0186	0.0230	0.0186	0.0245	0.0095	0.0049	0.0058	0.0027	0.0043	0.0026
234678 HxCDF	0.0217	0.0252	0.0181	0.0288	0.0098	0.0046	0.0049	0.0027	0.0031	0.0016
123789 HxCDF	0.0028	0.0036	0.0029	0.0037	0.0014	< 0.0010	< 0.0010	< 0.0010	< 0.0010	< 0.0010
1234678 HpCDF	0.0277	0.0333	0.0197	0.0404	0.0118	0.0086	0.0100	0.0040	0.0045	0.0028
1234789 HpCDF	0.0050	0.0048	0.0031	0.0081	0.0023	0.0014	0.0015	< 0.0010	< 0.0010	< 0.0010
OCDF	0.0070	0.0077	< 0.0050	0.0144	< 0.0050	< 0.0050	< 0.0050	< 0.0050	< 0.0050	< 0.0050
ng I-TEQ/Nm3 incl. ½ of DL	**0.0209**	**0.0262**	**0.0223**	**0.0258**	**0.0159**	**0.0061**	**0.0051**	**0.0051**	**0.0057**	**0.0036**

M = manual sampling system; M1 = manual sampling system 1; M2 manual sampling system 2
AMESA = long term sampling system

From Table 1 we can see that the results of the parallel measurements on a 8 hour basis shows a very good correlation between the reference manual sampling and the sampling using the long term system. For both stacks the results of the long term system were practical identical with the ones obtained with the manual reference sampling. In the case of stack 1 the variation between the results of the manual sampling (M1 = 0,0209 ng-TEQ/Nm3, M2 = 0,0262 ng-TEQ/Nm3) is much higher than the difference between the average manual

sampling results and the long term result (AMESA = 0,0223 ng-TEQ/Nm3). Despite the very low emissions of PCDD/F of stack 2 (in the range of 0,005 ng-TEQ/Nm3) and the difficulties in the quantifying of such low amounts we denoted the same good correlation of the results obtained with the two manual and the long term sampling system. For stack 2 M1 = 0,0061 ng-TEQ/Nm3, M2 = 0,0051 ng-TEQ/Nm3, AMESA = 0,0051 ng-TEQ/Nm3.
We found a similar correlation of the results also in the past using a DMS long term sampling system (Dioxin Monitoring System) on a municipal waste incinerator [5].
The 24 hour parallel sampling did not give the same good correlation on stack 1. But in this case we had only one parallel manual sampling result we could compare and the sampling time was beyond 8 hours for which the manual sampling system is validated. On stack 2 the emission values were at so low values, that we have a high associated uncertainty. From a practical point of view the results are nearly identically. Indeed the filed blank contribution can be close to 0,001 ng-TEQ/Nm3.

On the basis of the results we can give the following recommendations:
Long term measurement systems should be tested and validated by parallel measurements using a standard reference method like EN-1948 of US EPA 23.
By using contemporaneously two ore more manual reference sampling systems also a variation between the manual method can be estimated.
Parallel measurements of the long term sampling systems with the manual reference sampling should be done on a 6 to 8 hours sampling time in order to resemble sampling conditions used for the validation of the manual reference sampling.
For the validation of the long term sampling systems at sampling times exceeding 8 hours we suggest to perform in parallel several consecutive manual sampling of 8 hours. For example 3 to 5 consecutive manual sampling of 8 hours covers 24 to 40 hours of long term sampling. The obtained average results of the distinct manual samples can be compared with the result of the corresponding long term sampling.

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