Long-Term Sampling – A Method for Continuous Emission Monitoring of Dioxins/Furans and Mercury

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Introduction

The continuous emission monitoring of the different compounds which are emitted by industrial facilities is an important topic to approve the compliance to different regulations like WID. However, there are several compounds which cannot be measured in real time. Specific dioxins/furans (PCCD/PCDF) and other POPs (Persistent Organic Pollutants) cannot be measured by online monitors.

In any way the acceptance for continuous sampling of PCDD/PCDF as a good approach for continuous emission monitoring of these compounds increased over the last 15 years. In the meantime France followed the example of Belgium and demands by law the continuous PCDD/PCDF emission in all waste incineration plants. The increasing interest is also supported by CEN/TC 264 WG 1 which started a project to establish a standard for long-term sampling of PCDD/F and dioxin like PCBs (as EN 1948-5).

Beside the emissions of PCDD/PCDF there are other emissions of compounds which are not or not so easy to be monitored continuously. E.g. mercury can be monitored continuously, but for plants with low concentrations in the range of ug/m^3 the accuracies of the existing mercury CEMs depend very strong on the experiences and maintenance efforts of the operators. Otherwise the results are not accurate enough. Additional the availability of such systems is restricted. In the United States the new Portland Cement and the upcoming utility MACT rules accept besides the installation of mercury CEMs also the installation of continuous sampling systems for mercury.

This paper will give an overview of the experiences of around 15 years continuous sampling of PCDD/PCDF emissions with continuous dioxin sampling systems and the resulted success for the reduction of these emissions.

Additional it presents newest results of continuous sampling of mercury emissions in the low ug/m^3 range in industrial facilities.

Materials and methods

One system which is used for the continuous sampling of dioxin and furans is the AMESA system. The operating principles and functionality of the AMESA system were described in several publications[1,2] and have been proven through 15 years of long-term sampling of PCDD/F. In principle the used method complies with the cooled probe method of EN-1948-1 with the exception that the condensate flask is installed after the XAD-II cartridge and that therefore the condensate does not need to be collected and analysed. This is in accordance to US EPA method 23A. Additionally the plane filter for the dust collection is replaced by quartz wool included in the top of the XAD-II cartridge. The cartridge containing the adsorbed dioxins and furans is evaluated together with a data medium in an accredited laboratory. By means of this process, dioxins and furans are separated from the gas phase and the condensate in one adsorption step. With this method it is possible to collect the dioxin and furans up to one month on one XAD-II cartridge. Therefore the complete yearly dioxin emission of a plant can be determined.

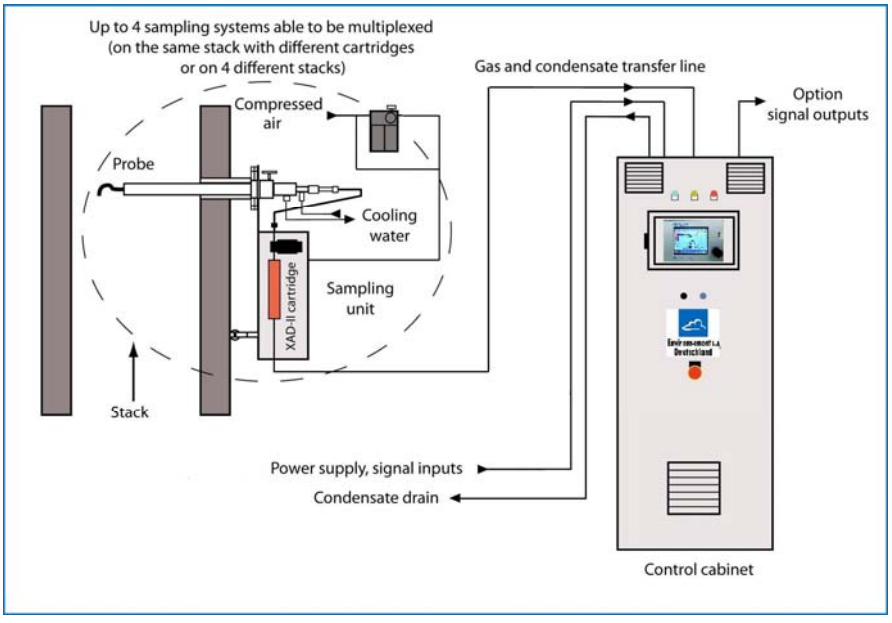

Fig. 1 Functional principle of the AMESA system

In Belgium the continuous emission monitoring of PCDDs/PCDFs is regulated in Flanders Vlarem II[3] and in Wallonia according a decree dated on 11th May 2000[4]. According to these regulations the PCDDs/PCDFs have to be sampled in a continuous way, with at least two-weekly analyses**.** For the thus obtained results a guide value of 0,1 ng TEQ/m³ is applicable. In the meantime the requirement of 2 weeks sampling was opened to a 4 weeks sampling if the concentration are permanently low and if the operator applies for it.
From the beginning it was important to generate reliable results and therefore it was developed in Flanders and published by Vito the "Code of good practice for approval of long term dioxin sampling equipment in stacks"[5].
This document describes several requirements on the used sampling system but also the conditions when a sampling should be realized. Specific during start-up and shut-down periods of the incinerator the sampling should be interrupted, because these phases of operation do not represent standard operating conditions.
Possible criteria to decide that the plant is in operation were defined as follows:
- a maximum oxygen concentration (18 %) in the flue gases of the combustion plant
- a minimum flue gas velocity through the chimney
- a minimum temperature in the (post) combustion chamber

Other but less indicated criteria, which cannot be applied as a sole trigger for operation of the continuous dioxin sampling, were defined as:
- feeding of waste
- movement of the grates
- decision of an operator to manually switch off the sampling.

In which distribution the different criteria are used by the operators is shown in fig. 3.
In Wallonia similar requirements were defined.
In the meantime France followed the example of Belgium. A decree dated 3rd August 2010[6] demands by law the continuous PCDD/PCDF emission in all domestic and hazardous waste incineration plants until the 1st July 2014. This law covers around 200 stacks, which will increase the total number of worldwide installed continuous dioxin monitoring systems to around 450 to 500 systems.
The system was also modified in the meantime for the application of mercury adsorption traps. With this modified system were realized validation tests against the standard reference method.

Results and discussion:

Dioxins and furans

With the help of the ongoing publication of the measurement data of the Wallonia region[7] it could be demonstrated earlier, that the total dioxin emissions were reduced up to a factor of 20 in comparison to the first year of continuous dioxin monitoring, still if the quantity of burned waste was more than doubled.
In Flanders all the results are not in the same way available for the public like in Wallonia. However also in this region it could be demonstrated the positive effect of continuous monitoring.
Vito generated an application report[8] in the year 2009. Actual all 13 plant operators who answered the questionnaire have installed in total 21 AMESA systems. On the question if the operators think that the use of a continuous dioxin sampling system is usefull 76 % answered with yes (Fig. 4).
This reflects very good the positive impression of the operators after using such systems for several years. Additional it confirms that the sceptic opinion which some operators have before the installation are not confirmed by the operation of the systems for several years. Contrary to the former doubts, the operators see as advantages the possibility to have an adequate check for the efficiency of flue gas cleaning, to have an early warning system for disturbances, to have an alarm function with prevention of calamities and to have a proof of innocence after high dioxin depositions measured by the environment agency.
Another topic of discussion is the operating cost of such systems. In Flanders some operators complained about the high analysis costs. However as it was published for Wallonia[9] the total costs for the network of 11 stacks were in the range of 1,00 € per ton waste. These are very reasonable costs for a high benefit for the environment.

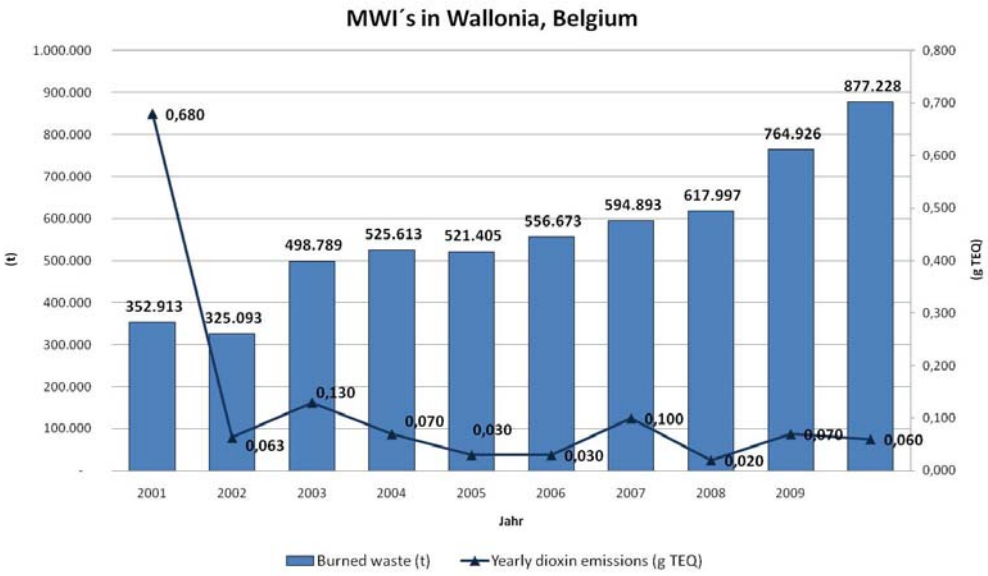

Fig. 2 Yearly balance of the Wallonia region 2000 - 2010

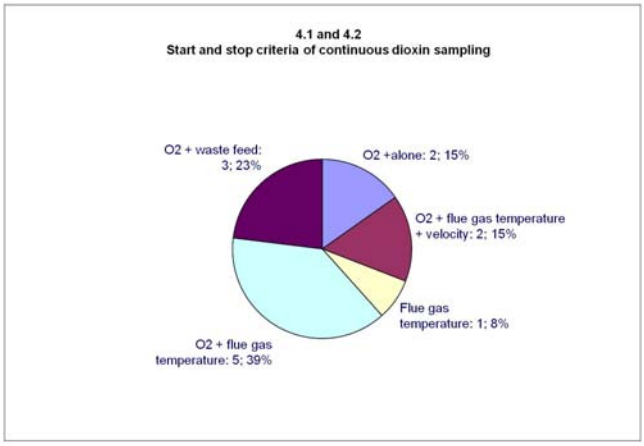

Fig. 3 Start and stop criteria in Flanders

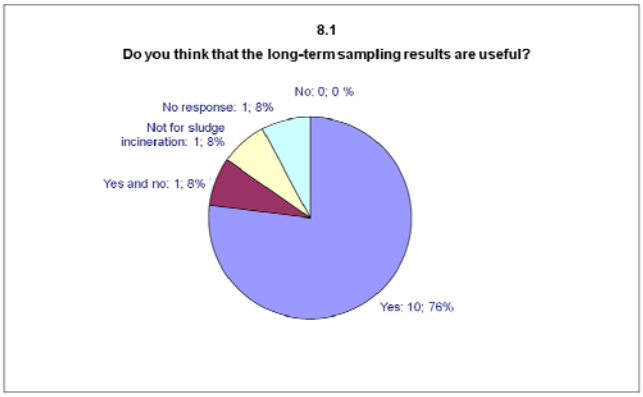

Fig. 4 Question 8.1 of the survey in Flanders

Mercury

There were realized several validation tests with the modified sampling system (AMESA M) on an industrial facility.

The results of the automatic sampling system comply quite good to the results of the MST. Beside this value the QA criteria for the relative deviation (RD) was fulfilled in all samplings and the recovery rate of the spike standard was between 97 % and 116 %.

The results demonstrated also that the measured concentrations of the Mercury CEMs showed systematic lower concentrations in comparison to the sampling methods.
The results of long-term sampling tests were also very promising (Table 1). The recovery of the spike standards were between 85,6 % and 93 %. By one trap the recovery was only 41,1 %. According to the trap supplier the reason for this low recovery could be the too high sampling probe temperature which was set to +180°C.
The breakthrough was between 0,03 % and 1,1 %.
By the calculation of the availability were considered time periods in which the sampling was interrupted during period of plant interruptions which are detected e.g. by too low flue gas velocities or too high O2 concentrations. The so calculated availabilities were > 99 % and with that quite better than the known availabilities of mercury CEMs. Also for the long-term sampling the measured results of the Hg-CEMs were systematic lower.

Date / Time	**AMESA M Trap 1 / Trap 2 [ug/Nm3]**	**Relative Deviation per PS 12 B RD = Abs(T1-T2)/(T1+T2) [%]**	**QA criteria per PS 12 B (RD < 10 %) fulfilled?**	**CEM [ug/Nm3] Average over sampling period**
11.02.2011 / 10:11 am to 14.02.2011 / 11:44 am Time total: 73:33 (hh:mm), Plant interruption time: 2:44 (hh:mm) Sampling time: 70:44 (hh:mm) **Availibilty: 99,9 %**	2,92 / 2,85	1,2	y	2,18
24.03.2011 / 09:02 am to 01.04.2011 / 07:44 am Time total: 190:42 (hh:mm), Plant interruption time: 0:02 (hh:mm) Sampling time: 190:30 (hh:mm) **Availibilty: 99,9 %**	1,22 / 1,01	9,6	y	0,83
01.04.2011 / 09:34 am to 04.04.2011 / 16:09 am Time total: 78:35 (hh:mm), Plant interruption time: 6:35 (hh:mm) Sampling time: 72:00 (hh:mm) **Availibilty: 100,0 %**	1,05 / 1,09	1,9	y	0,76

Table 1 Long term mercury sampling in comparison to the results of the mercury CEMs.

References:

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4. Arrêté du Gouvernement Wallon du 11 mai 2000, M. MICHEL FORET, Ministre de l'Environnement, de l'Aménagement du Territoire et de l'Urbanisme.
5. De Fré R., Wevers M (2002), *2002/MIM/R/125.*
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