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1996 TO 2016 – TWENTY YEARS OF APPLICATION AND EXPERIENCES WITH CONTINUOUS SAMPLING OF DIOXIN EMISSIONS

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Introduction

In 1996 started the type performance test of the first generation of AMESA systems with the finalization in 1997 and the publication in the Ministerial Gazette of the German Ministry of Environment in June 1998 [1]. The method which was and still is used in the AMESA systems and which was certified was the so called simplified cooled probe method which was introduced and published already in 1993[2].
The start of this type performance test in 1996 can be seen as the start of the commercial use of this kind of technology for the continuous emission monitoring of PCDD/PCDF emissions.
Due to the successful application and positive experiences, which were resulted by these applications this technology increased it application ranges in quantity and different kind of plants. This was supported by degrees in countries like Belgium[3,4] France[5] and Italy and leaded to approx. 450 installed long-term sampling systems only in Europe. Additional to these systems were installed 30 – 40 systems outside of Europe mainly in Asia and North America.
For Europe the success and acceptance was finally confirmed by the publication of the new normative standard CEN/TS 1948-5 for continuous sampling of PCDD/PCDF and dioxin-like PCB. This standard was published in April 2015 and is now the worldwide first standard for the continuous sampling of PCDDs/PCDFs and dioxin-like PCBs[6].
The existence of such a standard is surely a kind of minimum requirement for the ongoing process by the revision of the BAT (Best Available Technology) Reference document, also known as BREF document, for waste incinerators, which was started in May 2014 in Sevilla[7]. The continuous sampling of PCDD/PCDF emissions is in any way a topic, which is discussed seriously.
There were collected many results over these 20 years of sampling applications in different kind of plants. The collected results demonstrated in many cases the good operation of the plants and confirmed dioxin emission levels, which are in the range of less than 1 pg TEQ/Nm^3. This is surely a range, which cannot be confirmed and/or demonstrated by the standard reference method as during a few hours not enough dioxins and furans are selected to have concentrations higher than the detection limits. But the gained results demonstrated also in some cases that there can occur situations in which a plant which runs over many years with low dioxin emissions can have accidents and can therefore emit in 1 or 2 months more dioxins as normally over a period of 10 years. Such events and therefore such impacts on the environment cannot be detected by short term sampling of only several hours.
This paper will give an overview of such results and demonstrates in this way, how informative such systems are for the public and the authorities.

Materials and methods

The AMESA D uses the cooled probe method which is describes in CEN/TS 1948-5 (Fig. 1).

Figure 1 — Scheme of long-term sampling system based on cooled probe method

The important modification for long-term sampling by the cooled probe method (same by the filter/condenser method) is the fact that the condensate is filtered through the adsorption cartridge and discarded via the condensate flask unit. This means the condensate does not need to be collected and send to the dioxin laboratory for analysis. If this modification would not exist it would be not practicabel to use this method as in a 4 weeks sampling there could be collected several hundred liters of condensate. At all this modification is in compliance to US EPA method 23A which is used in the US for short term manual sampling.

Results and discussion

Starting in the year 1999 there was installed in Belgium a network of continuous dioxin sampler in all MWI´s (Municipal Waste Incinerators). In the Wallonia part of Belgium these results are published in the internet. The yearly dioxin emissions decreased during this period from 0.68 g TEQ to 0.03 to 0.04

g TEQ. This is a reduction by a factor of 20 – 30, even if the total burned waste increased during this time by a factor of approx.. 3 from 352,913 tonnes to 1,017,902 tonnes per year (Fig. 2). Such results demonstrate the positive impact of this kind of monitoring to the environment.

Fig. 2 Yearly balance of the dioxin emission in the Wallonia region

However, in exactly one of these plants there occurred a malfunction last year, which leaded to a monthly average concentration, which was more than 100 times higher as in normal operation (Fig. 3).

Fig. 3 Monthly average dioxin emission concentration, line 2 of MWI Liege

In April the spiral conveyor of the activated carbon feeding of this line was broken. Therefore, the injection of activated carbon to adsorb the dioxins of the flue gas stopped and the flue gas was coming into the stack like a non-dioxin-treated flue gas. It was not possible to realize this malfunction by one of the other installed emission monitors as e.g. the gas-analyzers or dust monitor. When the malfunction was identified and repaired the dioxin concentration were coming down to the standard level. However, in these two months of high dioxin concentration there were emitted from this stack more dioxins into the ambient air as it was normally emitted over a period of 10 years. This example demonstrates how important the continuous dioxin sampling could be. Such an event will be not detected by the usual short term dioxin sampling of 6 – 8 hours on 3 days per year. But it is surely of big interest for the public, the authorities and also for the inventory calculations to identify and to quantify such events.

In another plant, it could be demonstrated over more than 5 years that in a modern waste incineration plant the dioxin emissions can be kept below 5 pg WHO-TEQ/Nm^3 (except one value), whereby the most results were below 1 pg WHO-TEQ/Nm^3 (Fig. 4.). The lowest values were around 50 fg WHO-TEQ/Nm^3 and therefore the lowest dioxin emission concentrations, which were ever reported up to now. Thus, demonstrating a very good and efficient flue gas cleaning by a combination of activated carbon injection with a catalytic layer in an SCR catalyst tower.

Fig. 4 Results of 5 years dioxin emission monitoring in a modern MWI

In the MWI of Würzburg, Germany there was a big concern by a NGO in the neighbourhood, when there was the planning for the 3rd incineration line in the year 2000. As a compromise there was decided at this time to install an AMESA system in the 3rd line to have a long-term sampling for the dioxin emission monitoring. Nevertheless, the operator did not want to cover the costs for the sampling and analyses over the complete year. Therefore, it was accepted to fix the sampling quantity on 6 samples per year, whereby the major of the neighbour city defines by phone calls to the plant operator, when the dioxin sampling should be started and stopped. The selected sampling periods in this case vary from several days until several weeks.
Due to this kind of operation this incineration line is monitored more than 40 % of the yearly operating time (Table 1), whereby the operating costs per year for the long-term sampler including the analysing costs are in the range of the manual sampling which covers only 0,3 % of the yearly operating time. In any way also in this plant it could be demonstrated that with BAT it is possible to run a plant over many years with low dioxin emissions (Fig. 5) and in this way the operator received good acceptance by the neighbours, which were concerned at the beginning.

Fig. 5 Dioxin emission of the MWI – Würzburg with flexible monitoring solution

Conclusion:
The results, which were gained over this period of 20 years demonstrated well the good usage of such automatic samplers and the positive impact on the environment. But with the mentioned example of the MWI in Liege, it was also demonstrated that even in plants, which run for several years with very low dioxin emissions, that there could exists situations that the dioxin emissions can increase by a factor of 100. The monitoring of such events, even if they are short is in any way very important. As dioxins are one of the most toxic compounds, which are released to the environment, a better monitoring can be required, specific as the costs for the dioxin analysis dropped also over the last 20 years, so that the total

costs of such kind of monitoring are now reasonable. Specific if also flexible monitoring solutions are selected as e.g. in the case of the MWI in Würzburg.
The experiences, which were gained with the different monitoring networks, will hopefully ends in an implementation of this technology into the BREF documents for the incinerators in Europe and other regions.

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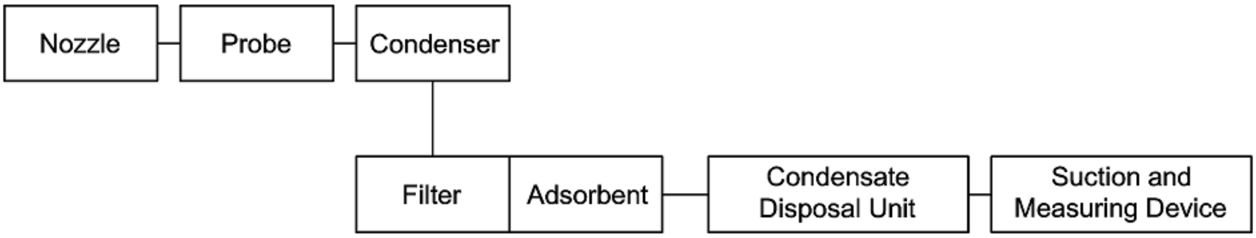

Figure 1 — Scheme of long-term sampling system based on cooled probe method

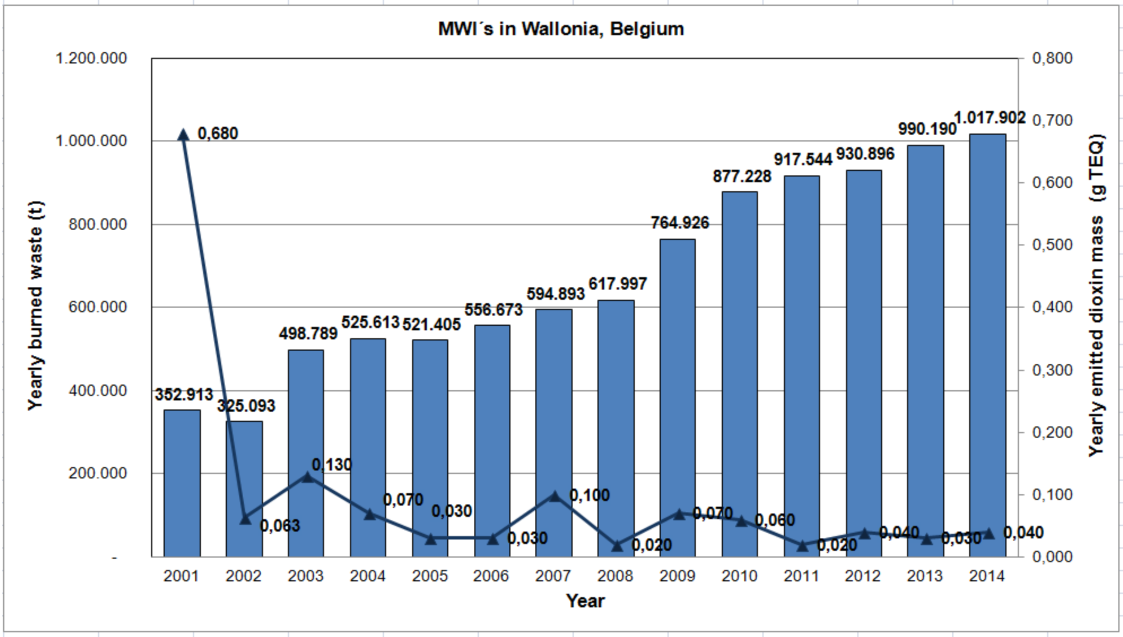

Fig. 2 Yearly balance of the dioxin emission in the Wallonia region

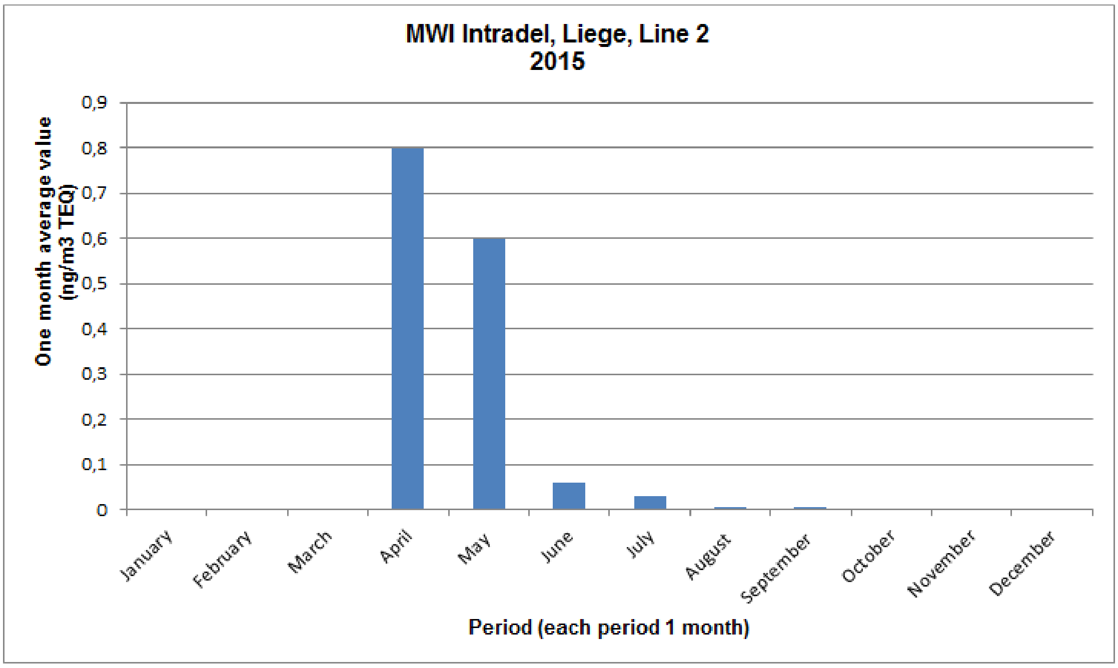

Fig. 3 Monthly average dioxin emission concentration, line 2 of MWI Liege

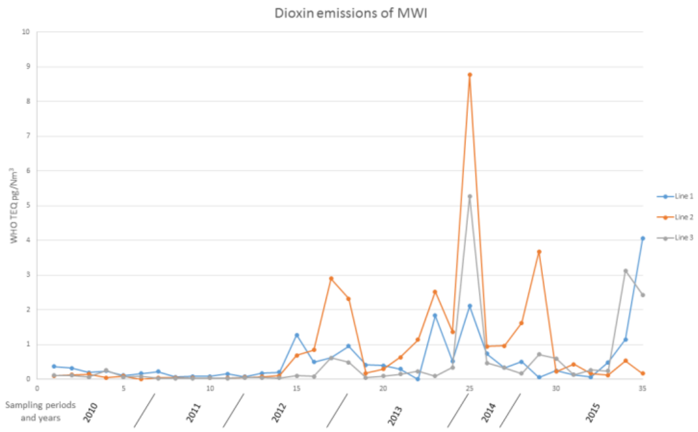

Fig. 4 Results of 5 years dioxin emission monitoring in a modern MWI

Year	Total yearly sampling period in [%]
2007	44
2008	39
2009	36
2010	36
2011	38
2012	42
2013	52
2014	42

Table 1: Yearly sampling period in the MWI Würzburg, with 6 samples per year.

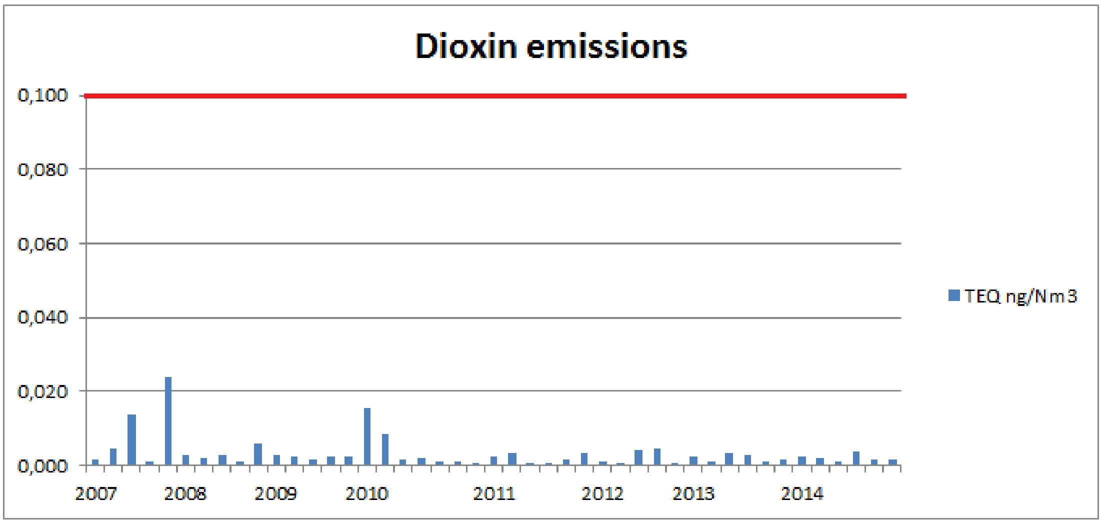

Fig. 5 Dioxin emission of the MWI – Würzburg with flexible monitoring solution