

CONTINUOUS DIOXIN EMISSION MONITORING- MEASUREMENT RESULTS OF EXTENDED APPLICATION RANGES

Reinmann J

Environnement S.A Deutschland, Benzstrasse 11, 61352 Bad Homburg, Germany

Introduction

Starting by degrees in Belgium in the years 1999 and 2000^{1,2} followed since 2004 in regions of Italy by granted operating licenses of regional authorities (Arpa) in regions of Italy and by a degree of August 2010 in France³, the continuous monitoring of PCDD/PCDF emissions of municipal waste incinerators (MWI's) was well introduced in Europe.

There were installed until now around 450 continuous dioxin samplers in Europe plus around 30 - 40 systems mainly in Asia and North America.

This increasing interest and application of the continuous dioxin monitoring was also supported by the work of the European TC264 WG1, which started to establish a standard as CEN/TS 1948-5 for continuous sampling of PCDD/PCDF and dioxin-like PCB. The first draft was provided to CEN and is for the moment under approval⁴.

In around 300 applications the continuous monitoring of the dioxin emissions was realized with the AMESA D system. As the application range is extended from standard MWI to other industrial facilities as e.g. steel and sinter plants it is important to determine the limits of application for such systems.

This paper will show some new results gained with the AMESA D system for higher dioxin concentrations, longer sampling periods of up to 6 weeks and higher adsorber cartridge temperatures. These results were also used to validate new limits as it is requested by the coming CEN/TS 1948-5.

Materials and methods

The operating principles and functionality of the AMESA D system were described in several publications^{5,6} and have been proven through almost 20 years of long-term sampling of PCDD/F. The used method complies with the cooled probe method of CEN/TS 1948-5. By this method the condensate flask is installed after the XAD-II cartridge and therefore the condensate does not need to be collected and analysed. That by the sampling in this way the amount of PCDD/PCDF in the condensate is negligible was demonstrated several times and approved e.g. in a TUV type performance test according the EU notified minimum requirements for continuous sampling systems in the years 1996/1997^{7,8} and the first realized QAL1 test of such a system in the year 2013⁹. The used method is also in accordance to US EPA method 23A. The requested dust filter is integrated in the adsorber cartridge which is filled with XAD-II, thus making the handling easy for the operator as only one part needs to be exchanged.

The cartridge containing the adsorbed PCDD's/PCDF's, PCB's and other POPs 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 6 weeks on one XAD-II cartridge. Therefore the complete yearly dioxin emission of a plant can be determined.

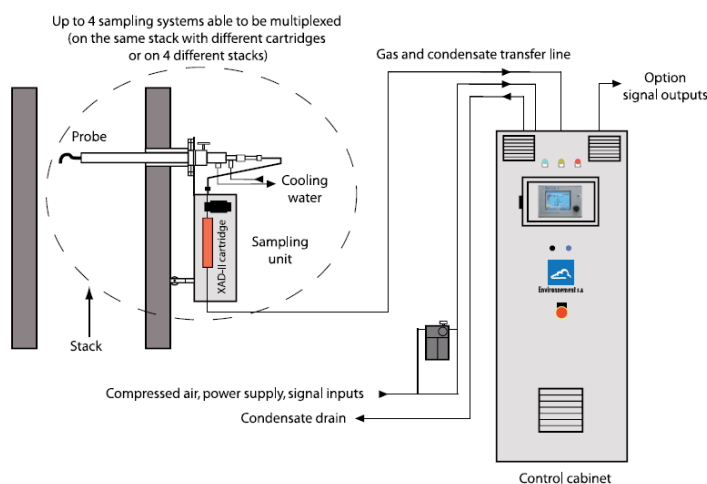


Figure 1: Functional principle of the AMESA system

In the coming CEN/TS 1948-5 is described a certification process which should be realized by each system which is foreseen as to be used for the application of dioxin emission monitoring. Even if the described tests were already realized and approved by the original AMESA system during the type performance test in

1996/1997 this certification was repeated with the AMESA D system by a QAL 1 test in the year 2013. The main interests for the new QAL1 test were the extension of the XAD-II adsorber cartridge temperature range, the maximum certified sampling period combined with a higher dioxin concentrations. This test was realized in a biomass combined heating facility. Therefore were installed 2 AMESA systems on the same stack. For validation measurements were done several short term samplings of 6 hours with parallel installed manual sampling trains (MST's) using the filter/condenser method according to EN 1948-1. For variations of the XAD-II adsorber cartridge temperature, the cartridge box in which the XAD-II cartridge is installed, was equipped with a heater to be able to heat up the cartridge to temperatures $> 50\text{ }^{\circ}\text{C}$. To determine the possible breakthrough by this higher adsorber cartridge temperature a second cartridge was installed outside of the cartridge box placed in a cooled water ($< 20\text{ }^{\circ}\text{C}$) bath. The plant operator varied the operating modes thus relating in a variation of the dioxin concentrations in the stack. In this way, maximum dioxin concentrations of 0.5 ng TEQ/Nm^3 could be realized.

One operator of another European Waste Incineration Plant wanted to monitor the dioxin concentrations in his raw gas also during the modification of some operating conditions. There was the request to realize sampling periods of maximum 2 weeks by expected dioxin concentrations of more than 10 ng TEQ/Nm^3 . The samplings should be realized on 3 different incinerations lines. As this project was limited from the beginning for a period of several months the efforts for an installation of 3 complete systems seemed to be too costly. For that the multiplex option of the AMESA D system was used. By this option it is possible to multiplex with one control cabinet between maximum 4 sampling probes. In the here described test with 3 sampling probes the system switched every 45 minutes from one duct to the other.

Results and discussion

The QAL 1 test was conducted over a period of 9 months and a total of 21 test runs were completed. The sampling durations were from 6 hours up to 6 weeks for the determination of breakthrough by the longest sampling periods.

The reproducibility between the two AMESA D systems was 16.9 % related to the limit value of 0.1 ng TEQ/Nm^3 (fig. 2). This is for dioxin measurement a quite good result.

For the breakthrough tests the XAD-II adsorber cartridges were heated up to $+50\text{ }^{\circ}\text{C}$. The measured breakthrough after 34 and 46 days showed values of maximum 0.3 % (see table 1.). Comparable results were gained over the years by several breakthrough tests also documented for higher XAD-II adsorber temperatures of $+50\text{ }^{\circ}\text{C}$ ¹⁰. The important topic this time was to validate this higher temperature of $+50\text{ }^{\circ}\text{C}$ of the XAD-II cartridge by an independent test institute as TUV Rheinland. After the successful finalization of the type performance test the AMESA D system was published as the first (and up to now in June 2014 only) QAL 1 certified system on the market.

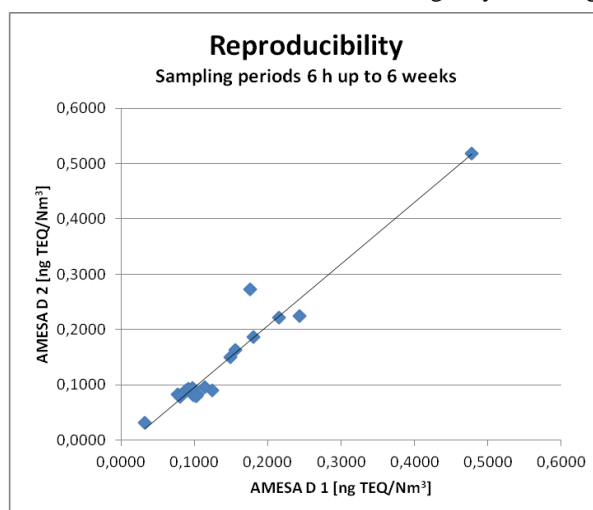


Fig. 2 Reproducibility of AMESA D 1 vs. AMESA D 2

Date	Sampling volume (Nm ³)	AMESA D 1 (ng TEQ/Nm ³)			AMESA D 2 (ng TEQ/Nm ³)		
		1 st cartridge	2 nd cartridge	Break-through (%)	1 st cartridge	2 nd cartridge	Break-through (%)
08.3. – 23.4.13	450	0.1020	0.00032	0.3	0.0800	0.00014	0.2
30.4. – 03.6.13	370	0.0974	0.00020	0.2	0.0938	0.00007	0.1

Table 1. Results of breakthrough tests by long-term sampling

For the raw gas measurements in the waste incineration plant it was important to determine first, if for such extreme conditions in comparison to standard stack gas conditions, a sampling of two weeks is possible. The stack gas conditions in the duct were dust concentrations from 5 – 25 mg/Nm³ with peaks of up to 1000 mg/Nm³, temperatures from 180 to 200 °C by a humidity of 19 Vol%.

The dioxin concentrations which were determined earlier by measurements with the SRM were more than 10 ng TEQ/Nm³. Specific for that it was important to check if a sampling of two weeks is possible without having breakthrough. Additional there was the risk if the peaks of high dust happened too often that the sampling probe or adsorber cartridge will be blocked after some days. In worst case it would be necessary to reduce the sampling period.

For this determination the start of the project was divided in two steps: at first it was done a sampling of one week followed by a sampling of two weeks. For both sampling was installed a second XAD-II adsorber cartridge in line to determine the breakthrough.

The temperature of the XAD-II cartridge was in average around +38 °C with peaks up to +42 °C and therefore below the former in the QAL1 test validated temperature of +50 °C.

The results of the breakthrough test are listed in table 2. Due to these positive results it was considered that a sampling of 2 weeks is possible under these extreme conditions.

Date	Sampling volume (Nm ³)	AMESA D (ng TEQ/Nm ³ at 11% O ₂ , dry)		
		1 st cartridge	2 nd cartridge	Breakthrough (%)
15.7. – 22.7.13	64,7	2.8	0.055	1.9
22.7. – 05.8.13	112,8	6.1	0.035	0.6

Table 2. Results of breakthrough tests in raw gas

Specific the breakthrough value of 1.9 % of the one week sampling was higher as normally known from former tests by lower concentrations. However, it was quite lower than 10 % as it is requested by EN 1948-1 and the coming CEN/TS 1948-5. It was therefore defined that a sampling of two weeks under the given raw gas conditions is possible.

Another topic was the question if there are streaks of dioxins in the duct as the available sampling ports did not fulfill the requirements of straight line before and after the sampling point. Therefore 3 sampling probes were installed in the duct on almost the same position with three different insertion depths of 0.5 m, 1.0 m and 1.5 m. The measured velocities at these three positions were 16.0 m/s, 12.3 m/s and 8.0 m/s respectively. Due to the different velocities which generate, due to the isokinetic extraction, different sampling flowrates, the sampled flue gas volumes were different on the three sampling points. For this measurement the system operated in the multiplex mode with a switching period of 2 hours between the sampling probes.

The measured dioxin concentrations at the different sampling points are listed in table 3.

Date	Insertion depth (m)	Gas velocity (m/s)	Sampling volume (Nm ³)	Concentration (ng TEQ/Nm ³ at 11% O ₂ , dry)
13.8. – 29.8.13				
Sampling point 1	0.5	16.0	49.2	2.1
Sampling point 2	1.0	12.3	39.0	1.7
Sampling point 3	1.5	8.0	27.3	0.9

Table 3. Results of multiplex sampling at three different insertion lengths

At the end of this sampling period the probe of sampling point 3 had some clogging problems. As possible reasons were expected the low sampling velocity due to the low gas velocity at this sampling point combined with the possible high dust load and the relative long switching period from probe to probe of 2 hours. With this operating mode on each probe it is not sampled for 4 hours. In such a case it is possible that dust which was entering the probe stuck in the probe additional due to the high temperature before the sampling starts again.

Taking into account the gained results, it was selected to use the insertion length of 1.0 m for the sampling on the 2 other incineration lines and to use a switching period of 45 minutes to reduce the risk for possible clogging of

the sampling probes. As sampling period were selected 14 days. This means on each cartridge was sampled maximum less than 5 days (14 days / 3) which assured to have no breakthrough.

With this operating mode it was sampled the following 6 months in parallel on the 3 incineration lines. The dioxin concentrations varied during this period between 1.1 and 14 ng TEQ/Nm³(fig. 3).

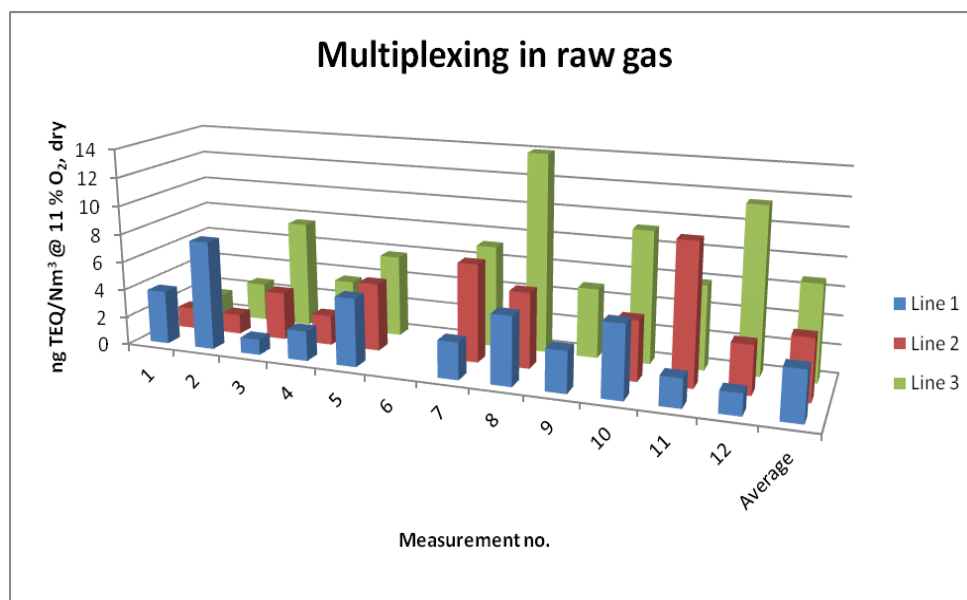


Fig. 3 Results of 6 months continuous sampling in raw gas in multiplex mode

With the new gained results it could be demonstrated that the use of the continuous dioxin sampler AMESA D can be extended also to other applications as the standard emission monitoring in MWI's. Beside this it was important also in accordance to the coming standard CEN/TS 1948-5 to validate in an official way the maximum XAD-II adsorber cartridge temperature of +50 °C, the maximum sampling period of 6 weeks by the maximum certified dioxin concentration of 0.5 ng TEQ/Nm³. Additional with the measurements in the raw gas of another waste incinerator the possible sampling in the concentration range of several ng TEQ/Nm³ could be demonstrated.

References:

1. Vlarem, www.lne.be, Departement Leefmilieu, Natuur en Energie.
2. Arrêté du Gouvernement Wallon du 11 mai 2000, M. MICHEL FORET, Ministre de l'Environnement, de l'Aménagement du Territoire et de l'Urbanisme.
3. Journal Officiel de la République Française, (2010) *Texte 10 sur 126, 21 août 2010*.
4. <http://standards.cen.eu>
5. Funcke W., Linnemann H. and Phillip Ch. (1993) *Chemosphere* 26: 2097-2101.
6. Becker E., Reinmann J., Rentschler W., Mayer J. (2000) *Organohalogen Compounds*; 49: 21-23.
7. Wilbring P, Gerchel B; TÜV report 936/805017B, 1997
8. Gemeinsames Ministerialblatt, Nr. 28, Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit, RdSchr.v.8.6.1998, Bundes einheitliche Praxis bei der Überwachung der Emissionen, 543 – 556, EU-Notification 97/26/D
9. http://www.gall.de/15267/0000033596_00_environment_Amesa_en.pdf
10. Reinmann J., Haag R., Löthgren C.-J., Weber R. (2008) *Organohalogen Compounds*; 70: 2074-2077.