# CEN TS/EN 1948-5 THE WORLDWIDE FIRST STANDARD FOR CONTINUOUS DIOXIN EMISSION MONITORING - GENERAL REQUIREMENTS AND TYPE PERFORMANCE TEST

Reinmann J

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

**Introduction**

In Europe the continuous monitoring of dioxin emissions by long-term sampling was quite well introduced during the last 15 years. Due to degrees in countries like Belgium[1,2] France[3] and Italy there were installed up to now approx. 450 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.

Due to this increasing interest and application of the continuous dioxin monitoring the Working Group 1 (WG 1) of the European TC264 established a standard as 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[4]. In this standard are listed several minimum requirements specific for the automatic continuous sampling of dioxins and it includes in the normative Annex C test requirements for a type performance test of such samplers.

The AMESA D system passed in 2013 a QAL1 test as it is requested in the EU for automatic measurement systems (AMS) and was published on 1st April 2014 by the German Ministry of Justice and Consumer Production as QAL1 certified[5]. The test requirements of this QAL test were in full compliance to the requirements listed in the normative Annex C of TS/EN 1948-5.

This paper will give detailed information about the listed minimum requirements and the type performance test of TS/EN 1948-5.

Additional this paper will show some results of a multiplex application in which were done parallel measurements in the raw gas and the cleaned gas of a municipal waste incinerator (MWI).

**Materials and methods**

The sampling methods for continuous dioxin sampling are described in TS/EN 1948-5 in chapter 5 and are as follows:

The sampling is done isokinetically in the duct for a long time period usually from 24 h up to several weeks, typically four weeks. The sample gas flow rate is automatically controlled. The PCDDs/PCDFs/PCBs, both adsorbed on particles and in the gas phase, are collected in the long term sampling system. Dependent on the sampling system, the sampling unit can consist of different compartments, e.g. filter, condensate flask unit, solid or liquid adsorbent. The systems are based on the following sampling methods, described in EN 1948-1:

— filter/condenser method;
— dilution method;
— cooled probe method.

Schematic representations of the sampling methods according to EN 1948-1 including the modifications for long-term sampling are given in Figure 1, Figure 2 and Figure 3.

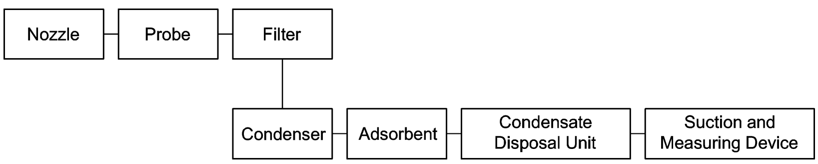


Figure 1 — Scheme of long-term sampling system based on filter/condenser method

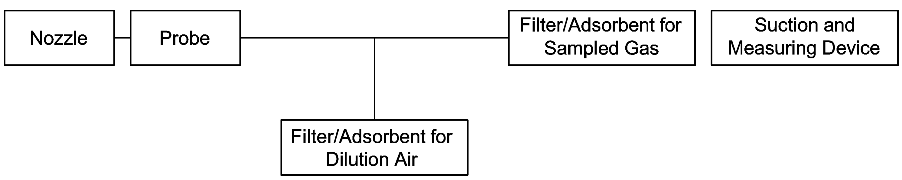


Figure 2 — Scheme of long-term sampling system based on dilution method

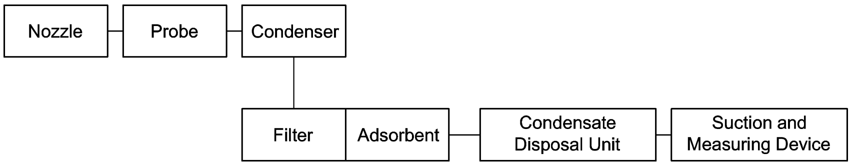

Figure 3 — Scheme of long-term sampling system based on cooled probe method

The important modification for long-term sampling by the filter/condenser and the cooled probe 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 these methods 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.
In chapter 7 of TS/EN 1948-5 are listed the "Minimum requirements for long-term PCDD/PCDF/PCB sampling methods". There is a request that the minimum requirements and method validation criteria shall be fulfilled by the manufacturer of the long-term sampling system and documented and checked during the type performance test which is part of the certification process (see EN 15267-1). To fulfill this, several criteria have to be fulfilled.

The operating principle and functionality of the AMESA D system were described in several publications[6,7]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 TS/EN 1948-5. 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.
In the normative Annex C of TS/EN 1948-5 are described "Performance criteria and test procedure for certification". With the AMESA D system such a certification was realized with the QAL 1 certification process. This QAL 1 test was realized in a biomass combined heating facility in which the flue gas cleaning consists of an Uria injection for the reduction of NOx, a Natriumbicarbonat injection for the SO2 reduction and activated carbon injection followed by bag filters for the dioxin reduction. There were installed 2 AMESA D 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 °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 °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.
In another appplication one operator of a European Waste Incineration Plant wanted to monitor the dioxin concentrations in his raw gas and parallel in the cleaned gas to check the dioxin reduction efficiency during different operating modes. It was demonstrated already in earlier projects[8] that the AMESA D system can be operated also by dioxin concentration of several ng TEQ/Nm$^3$. As the installation of 2 AMESA D systems would be too expensive for a test of several weeks the operator preferred to use a system with multiplex option. By this option it is possible to multiplex with one control cabinet between maximum 4 sampling probes. In the here described test with 2 sampling probes, one in raw gas and one in cleaned gas, the system switched every 2 hours from raw to cleaned gas.

**Results and discussion**
In table 1 are listed several of the requirements of TS/EN 1948-5 and the realization with the AMESA D system due to its design and the results gained during the QAL 1 test. 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.

| Requirement | Result |
|---|---|
| With each sampling equipment a validation trial shall be carried to specify the maximum sampling period (usually 2 weeks or 4 weeks). This trial has to be performed in order to validate the sampling efficiency and the long-term behavior of the system for the specified measurement periods. | The maximum sampling period was 6 weeks. The maximum breakthrough was 0.3 % (see table. 2). |
| In the case of using two or more probes, it shall be ensured that the unused probes are protected against contamination or cleaned before use, if exposed for long time to stack atmosphere. | Not applicable as the AMESA D system uses one probe. |
| In case, XAD-2 is used, the XAD-2 cartridge shall be mounted in a vertical direction in order to avoid channeling. Additionally, the flue gas shall flow from top to bottom of the XAD-2 cartridge. | Confirmed. |
| The filter efficiency shall be higher than 99.5 % on a test aerosol with a mean particle diameter of 0.3 µm, at the maximum flow rate anticipated (or 99.9 % on a test aerosol of 0.6 µm mean diameter). | Confirmed. Filter efficiency of 99.9 % for an aerosol of 0.6 µm mean diameter confirmed |
| The overall deposits in the sampling train shall be determined at the end of the intended sampling duration (typically 4 weeks). More than 90 % of the total I-TEQ and WHO-TEQ respectively shall be found in the analyzed compartments of the sampling train. This means that less than 10 % of total I-TEQ/WHO-TEQ are acceptable to be found in the sum of the breakthrough sample and in all compartments not analyzed in routine measurements. The breakthrough test shall be performed covering the intended sampling duration using a second sampling unit in series. | Confirmed. The total losses (sampling probe, breakthrough and condensate) for the long-term sampling were below 10 %. |
| If the maximum temperature of the sampling gas (filter/condenser method: 125 °C; dilution method: 40 °C; cooled probe method: 20 °C) is exceeded it shall be validated. This validated temperature shall not be exceeded during sampling. | During the QAL 1 test a max. cartridge temperature of + 50 °C was validated (table 2). |
| A leak check shall be performed before and after each sampling. | Confirmed. |
| A validation trial shall be carried out to demonstrate the comparability of the long-term method against the standard reference methods. | 15 comparison sampling were realized. |

Table 1. Minimum requirements of TS/EN 1948-5 and results of AMESA D system

Additional minimum requirements for individual systems are given to avoid increase of uncertainty.
1) Filter/condenser method
— The probe temperature shall be adjusted to a temperature higher than the water dew point.
— The filter shall adjusted to a temperature below 125 °C in order to avoid chemical reactions on activated surfaces and shall be kept over the dew point to avoid condensation.
— The condensate shall pass through the adsorbent.
2) Dilution method
— Dilution air shall be filtered using a filter system with 99.5 % efficiency for 0.3 µm particulates and with efficiency > 90 % for PCDDs/PCDFs/PCB. The filter system has to be exchanged at least once a year.
— The probe temperature shall be adjusted to a temperature higher than the dew point.
3) Cooled probe method
— The condensate shall pass through the sampling unit.

| 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 2. Results of breakthrough tests by long-term sampling

The results of the parallel measurements in raw gas and cleaned gas of a European Municipal Waste Incinerator are shown in table 3. The switching period between the raw gas sampling probe and the cleaned gas sampling probe was 2 hours. The results showed that the total dioxin reduction rate is too low to keep the limit value of 0.1 ng TEQ/Nm$^3$ and it could not be found any solution for it for the demonstrated measurement campaign.

| Date | Sampling volume raw gas (Nm3) | Sampling volume cleaned gas (Nm3) | Raw gas (ng TEQ/Nm$^3$) | Cleaned gas (ng TEQ/Nm$^3$) | Reduction efficiency (%) |
|---|---|---|---|---|---|
| 18.9. - 26.9.14 | 38.46 | 26.12 | 4.58 | 0.48 | 89.5% |
| 26.9. - 3.10.14 | 41.28 | 28.79 | 4.16 | 0.41 | 90.2% |
| 27.10. - 3.11.14 | 36.49 | 25.49 | 4.79 | 0.35 | 92.6% |
| 3.11. - 10.11.14 | 39.30 | 27.19 | 4.10 | 0.35 | 91.5% |

Table 3. Results of dioxin reduction efficiency under variable operating conditions

There could be only obtained a reduction of the dioxin concentration in the cleaned gas by 27 % (from 0.48 ng TEQ/Nm$^3$ to 0.35 ng TEQ/Nm$^3$). Due to these results it is planned a second measurement campaign in the plant.

**Conclusion:**

With TS/EN 1948-5 was published the worldwide first international standard for continuous dioxin sampling of flue gas emissions. This confirmed the increasing interest in Europe to get more information about the real yearly dioxin emissions of a plant which is also demonstrated by more than 450 installed systems in Europe. In Europe the emission control and the definitions of emission limit values (ELV´s) is regulated in the Industrial Emission Directive (IED) 2010/75/EU[9]. One important instrument for the emission control is the so called BREF-documents. These documents which need to be reviewed every 8 years define new limit values depending on the actual Best Available Technologies (BAT). The revision of the BREF documents for the incineration facilities started last year. Due to the already high quantity of installed dioxin samplers in Europe the continuous sampling of dioxin emissions is one important topic of the discussions. Due to the publication of TS/EN 1948-5 there exists now also a normative basis for future regulations.
The multiplex option of the AMESA D system could be demonstrated well in a parallel raw and clean gas sampling. This demonstrates that the system could be also well used for the optimization of flue gas cleaning devices and/or operating modes.

**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 Francaise, (2010) *Texte 10 sur 126, 21 août 2010.*
[4] http://standards.cen.eu
[5] http://www.qal1.de/15267/0000033596_00_environnement_Amesa_en.pdf
[6] Funcke W., Linnemann H. and Phillipp Ch. (1993) *Chemosphere* 26: 2097-2101.
[7] Becker E., Reinmann J., Rentschler W., Mayer J. (2000) *Organhalogen Compounds*; 49: 21-23.
[8] Reinmann J. (2014) *Organhalogen Compounds*;
[9] Industrial Emission Directive 2010/75/EU, http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=OJ:L:2010:334:TOC