Validation of a PCDD /Fs long-term emission sampling system at a large sinter plant for assessment of compliance to permitted Emission Limit Values

Esposito V[1], Bruno D[1], Maffei A[1], Giua R[2], Nicosia A[2], Ficocelli S[2]

[1] ARPA PUGLIA, Environmental Protection Agency of Apulia, Department of Taranto, Via Anfiteatro 8, 74100 Taranto, Italy.
[2] ARPA PUGLIA, Environmental Protection Agency of Apulia, Regional Air Quality Centre, Corso Trieste 27, 70126 Bari, Italy.

Introduction

Continuous sampling of emission into air of dioxins has been one of the targets of Directive 2010/75/EU Of The European Parliament And Of The Council on industrial emissions (Integrated Pollution Prevention and Control, IED Directive) since year 2010 [1]. It was stated that as soon as appropriate measurement techniques are available within the Union, the Commission shall, by means of delegated acts set the date from which continuous sampling of emissions into the air of heavy metals and dioxins and furans are to be carried out. Even earlier in 2005 [2], systems for long-term sampling were available and described as a very useful tool to get information on the total emitted mass over the sampling period compared to conventional manual sampling methods that cover only a short time (1-3 days) of the operating period and unable to intercept occasionally higher PCDD/F emissions that may occur and pass along as not detectable. One of the available equipments was tested at a sinter plant in Austria [3] were the local authority required continuous PCDD/F monitoring for some months after more stringent emission limits entered into force for the plant and proved to be successful.
PCDD/F in exhaust gas emissions samples were determined by the Environmental Agency of Apulia for a sinter plant located in Taranto (Italy) starting from June 2007 [4].
The present experiment was carried out between 2013 and 2014, aimed at verifying the applicability of a long-term sampling system at the sinter plant of a large steel works in Taranto, Southern Italy, and to perform its validation compared to the standard reference method (SRM). For the planned activities, a technical operational protocol was designed under the management and supervision of the Italian Ministry of the Environment.

Materials and methods

Short-term (6 hours) stack emission samples were collected according to Method UNI EN 1948-1 (filter condenser method) by using an Isostack apparatus (TCR Tecora, Corsico Milan, Italy). The filter-condenser method allows sampling of both gas-phase and particle-phase matter. The flue gas enters the sampling train through an electrically heated glass lined probe. This is connected to a glass filter casing in which a quartz fiber filter (Munktell, Baresnstein, Germany) is supported on a PTFE filter holder. The filter casing is inside an electrically heated box. It is followed by a water cooled coil condenser and a XAD-2 resin (Supelco, Supelpak, St Louis MO USA) filled cartridge. The condensate and the gas passes through the resin to a round bottomed flask in which the condensate is collected. Exhaust gases were drawn in isokinetic conditions from plant stack for a total of 6 hours.
Long-term sampling (7, 15, 30 days) samples were collected by using an DECS apparatus (TCR Tecora, Corsico Milan, Italy). The filter-condenser method allows sampling of both gas-phase and particle-phase matter. At the time of this experiment the EN 1948-5 method was not yet published even not in TS form.
Sample extraction was performed by Accelerated Liquid Extraction (Dionex, Sunnyvale CA USA) with Toluene. Extracts aliquots for the determination of PCDD/Fs and PCBs by method EN 1948 -2-3-4 were purified/fractionated by means of an automated clean-up process with a PowerPrep system (Fluid Management System, Waltham, Massachusetts) using disposable columns (multilayer silica, alumina and carbon). Extract aliquots for the determination of PAHs were purified over silica gel. Labeled standards were purchased from Cambridge Isotope Laboratories (Andover MA, USA) and used according to Method EN 1948 1-2-3-4 for PCDD/Fs and PCBs and ISO 11338 1-2 for PAHs. PCDD/Fs were separated by high resolution gas chromatography (HRGC) on a DB-5 MS capillary column (60 m x 0.25 mm, 0.25 µm film thickness, J&W Scientific, California). Isotope-dilution high-resolution mass-spectrometry determinations (HRMS) were carried out on a DFS High Resolution system (Thermo Fisher, Bremen, Germany) at a resolution of 10000 operating with electron ionisation (EI) at 45 eV in the selected ion monitoring (SIM) mode. PCBs including dioxin-like PCBs (dl-PCBs) were separated by HRGC on a HT8 capillary column (60 m x 0.25 mm, 0.25 µm film thickness, SGE Analytical Science, Australia) and determined by HRMS, in the same operating conditions used for

PCDD/Fs. PAHs were separated by HRGC on a DB-5 MS capillary column (30 m x 0.25 mm, 0.25 µm film thickness, J&W Scientific, California) and determined by HRMS, in the same operating conditions used for PCDD/Fs. For each batch of seven samples a laboratory blank and a control sample (certified fly-ash from inter-laboratory proficiency tests) were analysed. In addition, every sampling campaign included a field blank, according to UNI EN 1948-1 that were used to to ensure that no significant contamination had occurred during all steps of the measurement, and were not subtracted from measured values. Recovery rates for sampling and extraction labelled standards were in compliance with UNI EN 1948 requirements (grater than 50%).
Toxic equivalent (TEQ) values for PCDD/Fs were calculated using NATO Toxic Equivalency Factors (I-TEFs, 1989) as required by Italian legislation on stack emissions and expressed as lower-bound concentrations. Toxic equivalent (TEQ) values for PCBs were calculated using WHO Toxic Equivalency Factors (WHO-TEFs, 1998). The laboratory has ISO17025 accreditation.

Results and discussion
The validation protocol defined four stages for the validation of the experimental results: 1. Survey of the instruments available in the market for dioxins continuous sampling and definition of the most appropriate configuration for the plant. 2. Testing and evaluation of the sinter emission parameters aimed at selecting the best sampling configuration. 3. Testing of the continuous sampling system selected for the stack of the sinter plant. 4. Evaluation of the feasibility of the dioxin continuous sampling system with data validation.
The evaluation of the representativeness of the PCDD/F data collected from the continuous system (DECS) was made by comparing the data obtained by parallel manual sampling performed according to the standard reference method UNIEN1948-1:2006. In particular, continuous sampling together with parallel manual sampling were carried out, alternating DECS short-term sampling (6-8hours) and parallel manual sampling, with an overall number of 80 samples which were collected and analyzed by two different laboratories, including ARPA Puglia own testing laboratory. The following Table displays the results where LAB A was the test laboratory contracted by plant owners.

Table 1. External variability for parallel short-term sampling				
Sampling date	**ARPA**	**LAB A**	**|Δ|**	**u.m.**
10/10/13	0.123	0.111	0.012	*ng I-TEQ/Nm3*
29/10/13	0.032	0.035	0.003	*ng I-TEQ/Nm3*
20/11/13	0.080	0.030	0.050	*ng I-TEQ/Nm3*
10/12/13	0.097	0.057	0.040	*ng I-TEQ/Nm3*
03/01/14	0.048	0.057	0.009	*ng I-TEQ/Nm3*
21/01/14	0.029	0.028	0.001	*ng I-TEQ/Nm3*
12/02/14	0.037	0.016	0.021	*ng I-TEQ/Nm3*

As shown, the external variability (corresponding to the reproducibility according to ISO 5725-2:1994vi) determined as the maximum difference to be expected with a 95 % statistical confidence between the results of two laboratories measuring the same sample gas, each using their own individual sampling train and laboratory facilities and fulfilling the requirements of the UNI EN 1948-1 European Standard, has proven to be acceptable (± 0,050 ng I-TEQ/Nm3 as stated in UNI EN 1948-1 paragraph 14.3).
Concerning the validation testing of the continuous sampling system selected for the stack of the sinter plant, a number of two weekly short-term samples were performed in parallel with medium-term (15 days) and long -term (30 days) for a period of six months. The results are shown in a graphical form in the following Figure 1 and show excellent agreement for values ranging from 0,050 to 0,200 ngI-TEQ/Nm3 thus aound the level of interest that could be considered to be at 0,1 ngTE/Nm3 as stated in

the IED Directive.

Figure 1. results for parallel short and long-term stack emission sampling

The results obtained from the comparison between the continuous sampling system, both in the medium term (15days) and the long term (30days), and the standard manual method, showed the compatibility of the two systems for the assessing compliance of dioxin emissions to permitted emission values.
The compatibility of the results has also been tested on the short- term data produced by ARPA Puglia (manuals 6-8 hours) in parallel with the DECS sampling (6-8 hours).
It was therefore possible to state the full feasibility of long-term sampling of PCDD/F stack emissions E312 of the ILVA plant in Taranto. This results were approved by the Technical Committee set up by the Italian Ministry of Environment and as of today long-term sampling has been enforced into the Permit for the sinter plant.

References
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