

## Comparative and validation PCDD/F-measurements with different sampling systems

**Günter Bröker**

Landesumwelt Nordrhein-Westfalen (*State Environment Agency*)

Wallneyer Str. 6, 45133 Essen, Germany

### INTRODUCTION

PCDDs/PCDFs enter the environment via emissions from a wide range of sources and with use of materials and products contaminated with them. Due to the high toxicity of these compounds some European countries have regulated the concentration levels of PCDDs/PCDFs in waste gas emissions into the atmosphere from municipal and hazardous waste incinerators. These regulations have taken on various forms, including the limit of 0.1 ng I-TEQ/m<sup>3</sup>, the limit of 1 ng I-TEQ/m<sup>3</sup> connected to a guide value of 0.1 ng I-TEQ/m<sup>3</sup> or the requirement to use the state of the art on emission minimisation techniques in order to reduce dioxin emissions.

The council of the European Communities (EC) drafted a directive for Hazardous Waste Incineration with the aim to harmonise the legal regulations of the EC-member countries. Therefore the CEN/TC 264 "Air Quality" (European Standardisation Organisation) was charged with the elaboration of an European Standard (EN) describing a measurement procedure, to be applied as a reference method for the determination of PCDD/F concentrations below 0.1 ng I-TEQ/m<sup>3</sup> in the emissions of stationary hazardous waste incineration plants. The existing national standards, drafts or predraft standards of several countries were taken as a basis for this work, however all measurement methods, described in these guidelines had been validated only at emission concentrations above 1 ng I-TEQ/m<sup>3</sup>.

The CEN-working group prepared three standards comprising of: sampling, extraction and clean up and identification and quantification.

To evaluate the standards a comparative and a validation measurement were performed.

### SHORT DESCRIPTION OF THE PROPOSED MEASUREMENT SYSTEMS IN THE DRAFTED CEN-STANDARD

At the beginning of the standardisation work 17 more or less different sampling systems existed in Europe. To ensure a wide variety of applicability the working group decided to divide the 17 sampling systems into three groups according to different sampling principles (fig. 1). These were the

- Filter/condenser method
- Dilution/adsorber method
- Cooled probe method

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All sampling methods are extractive. In order to obtain a representative sample the sampler nozzle must be placed in representative positions in the duct cross section and the sampling must be carried out isokinetically. The sampling train is spiked with  $^{13}\text{C}$ -labelled standards before sampling to measure the sampling performance.

## **Filter/Condenser Method**

The particle-filter made from quartz or glass fibre is placed downstream the nozzle or after the probe. This filter with a minimum retention efficiency of 99,5% for a test aerosol with a maximum abundance at a particle diameter of 0.3  $\mu\text{m}$  has to be kept below 125 °C, but above the water dew point. In case of heavy dust loading, a quartz wool filter or a cyclone may be adapted before, so that the particle-filter is not overloaded. Downstream, a condenser is attached. The sample gas is cooled to below 20 °C. The gaseous and aerosol parts of the PCDDs and PCDFs are captured by impingers and/or solid adsorbents.

A modified system with division of flow differs in that after particle-filtering there is a flow divider. The main stream with a high volume flow to handle the isokinetic conditions passes the particle-filter. The side stream after flow division is identical to the device with condenser and adsorber unit described above.

## **Dilution method**

The sample gas is collected via a probe which has been heated to the temperature of the waste gas or even higher. The waste gas is cooled very rapidly to temperatures below 40 °C in a mixing channel using dried, filtered and, if appropriate, cooled air. The dilution avoids the temperature of the sampling gas falling below the dew point of water.

A glass fibre filter, fulfilling the same requirements like for the filter/condenser method, is used to collect the particulate PCDDs/PCDFs contained in the diluted waste gas stream. For the separation of the gaseous PCDDs/PCDFs a solid adsorbent is linked downstream.

## **Cooled probe method**

Different systems of this variant are possible. The sample gas passes the nozzle and a water-cooled probe.

The sample gas is cooled below 20 °C. The condensate is caught in a condensate flask. Downstream, impingers and/or solid adsorber units are linked in order to collect the gaseous PCDDs/PCDFs. Before the last impinger or solid adsorbent, there is a quartz or glass fibre filter to separate small particles and to break aerosols.

In the drafted European Standard, main performance criteria and quality criteria were laid down. In addition, examples of approaches which enable the performance criteria to be achieved will be given. Detailed descriptions of the sampling methods as well as tried and tested analytical procedures with their performance characteristics will be given as appendices. In this way, a precise description of the method is offered yet the user of the standard is allowed some flexibility to make changes to suit particular circumstances - as long as the main performance criteria are met. In this way future developments in sampling or analytical techniques are not discouraged.

## MEASUREMENT

In order to test the equivalency of the three sampling systems, a so called comparative measurements was performed. Although the analysis of emission samples for PCDD/F is well tested and has been the subject of many Round Robin Tests, the analysis should be part of the comparative test, but not as extensive as the sampling.

In a following measurement validation tests were performed to determine the performance characteristics of the measurement methods.

### Comparative Measurement

The comparative measurement was performed at a municipal waste incinerator equipped with an active coke-fixed bed. A sampling position inside a horizontal duct was chosen, which enabled all six sampling teams (two different measurement institutes used the same sampling method) to take samples in the same stretch of the duct. The duct had to meet normal sampling position criteria e.g. a straight lengths of duct. Sufficiently far away from any bends, dampers or other obstructions. All probes were divided into two equal parts and analysed by two analytical institutes. The analytical institutes are characterised with H and F in figure 3.

Pre-measurements characterised with LIS in figure 2, and 3 yields emission-concentrations in a range of 0.06 ng I-TEQ/m<sup>3</sup>.

Some results of the comparative measurement are shown in fig. 2, and 3. One measurement institute, charged by the owner of the MWC, additionally measured parallel in the same time; these results were not part of the comparative measurement. This institute is characterised with H in figure 2, and 3.

The result of the first measuring day varied more than those of the second day. The reason was much higher concentrations obtained by sampling system A. To decide whether the measurement A had to be regarded as an outlier or not, a statistical test according to Dixon was carried out. For a confidence probability of 95 % a test value of 0.896 and 0.912 was obtained for the results of sampler A quantified by both analytical laboratories. This is much higher than the lower outlier limit of 0.560 valid for 6 measurements. This result shows clearly that sample A from the first day has to be considered as an outlier. Therefore, it was excluded from the statistical calculations of the results of the first day. However, the decision to exclude the measuring results of sampler A of the first day does not mean that sampler A is not comparable with the others. First, the results of the second day from sampler A were in accordance with the others. Second, a parallel sampling was carried out on the first day using another sampler A. The results of this measurement were comparable with the other samplers. However, this sample was not part of the comparison measurements and was not quantified by the two analytical laboratories either. Therefore, it cannot replace the original measurement at day 1.

Deviating single measurements are a well-known problem in ultra trace analysis where amounts down to 10<sup>-12</sup> g have to be measured. The risk of contamination is always present and can never be excluded. The reason for the deviation was not possible to find out, but could be: Contamination during transport or mounting at site (not very well protected from outside influences) or contamination during extraction of the sample (a blank of the extraction apparatus previous to the extraction of sample A, first day is not available). Problems caused by clean-up or quantification can be excluded since both analytical laboratories found similar results (fig.3).

Nevertheless the working group experts concluded that the range of results found was acceptable in view of both the low concentrations being measured and the results of similar trials carried out in the

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past at higher concentrations. This allowed the conclusion that all three sampling methods yield comparable results. Results of the two analytical laboratories were also within the expected limits and therefore acceptable.

The results calculated on the basis of sampling spikes are comparable for all three sampling methods. However, because of the unknown behaviour of the sampling spikes compared to that of the native PCDDs/PCDFs in the sampling train, the sampling spikes should be used only as a check of the sampling efficiency and not for quantification. It will be required in the standard that the average recovery of the standards during sampling exceeds 50 percent.

## **Validation Measurement**

The validation measurement was performed at three different municipal waste incineration's (Austria, Germany) with different gas cleaning systems.

Validation A was carried out at an incinerator equipped with a full scale gas cleaning system including an active coke-fixed bed (the same plant as for the comparative measurement); the plant for validation B was equipped with a flue gas cleaning system including an electrofilter, a double stage wet scrubber and a catalytic unit for deNOX and dioxin destruction. As a result of the unsatisfactory validation measurement at plant A, additional similar measurement were performed at a municipal waste incinerator (plant C) equipped with a gas cleaning system for dioxin separation consisting of a lime/coke injection before the electrofilter.

In the validation tests, the reproducibility of the systems and the complete measurement methods used were assessed by taking duplicate samples. Measurements were carried out in such a way that each sampling team representing one sampling method performed the two duplicate samplings at the same time with two identical sampling trains. The PCDD/PCDF collecting material was extracted by the relevant sampling team. The clean-up and quantification steps, however, were performed (sample distribution on a random basis), by six European analytical institutes and one additional institute for analytical cross checks. The two samples of each duplicate measurement were analysed in most cases by the same analytical laboratory. All the institutes involved in sampling and analysis used the same spiking and calibration solutions.

The different sampling systems are comparable as was shown in the comparative measurements.

For some probes cross checks were performed. This means one half on the extract was sent to another lab for analysing. It was a random choice for the cross check probes but values with high detection limits were cross checked additionally.

All measurement results which not fulfils the minimum requirements of the standard were rejected from the statistical evaluation.

## **Internal variability**

The internal variability (corresponding to the repeatability) is determined as the maximum difference to be expected (with a 95 % statistical confidence) between the results of one measurement institute measuring in accordance with the requirements of the standards with two identical sampling trains the same sample gas, and using the same laboratory facilities.

The internal confidence interval for the dilution method was on a level of 0.19 (plant A)  $\pm 0.12$  ng I-TEQ/m<sup>3</sup>, on a level of 0.10 (plant C)  $\pm 0.08$  ng I-TEQ/m<sup>3</sup> and on a level of 0.04 (plant B)  $\pm 0.016$  ng I-TEQ/m<sup>3</sup>.

The internal confidence interval for the filter/cooler was on a level of 0.04 (plant A)  $\pm 0.06$  ng I-TEQ/m<sup>3</sup> and on a level of 0.03 (plant B)  $\pm 0.014$  ng I-TEQ/m<sup>3</sup>.

The internal confidence interval for the cooled probe method was on a level of 0.04 (plant B)  $\pm 0.011$  ng I-TEQ/m<sup>3</sup> and on a level of 0.13 (plant C)  $\pm 0.02$  ng I-TEQ/m<sup>3</sup>.

## External variability

The external variability (corresponding to the reproducibility) is determined as the maximum difference to be expected (with a 95 % statistical confidence) between the results of several institutes measuring the same sample gas each, using their own individual sampling train and laboratory facilities each, fulfilling the requirements of the standards.

For the performed tests at plant B, the external confidence interval is 0.05 ng I-TEQ/m<sup>3</sup> at the level of 0.035 ng I-TEQ/m<sup>3</sup>.

## SUMMARY

The perception of our investigations is summarised in some general observations:

- When checking the limit value of 0.1 ng I-TEQ/m<sup>3</sup>, the traditional sampling systems (e.g. EPA-5, modified) reach their limits. Measurements have to be done very carefully with very clean equipment.
- The application of sampling spikes as reference values yields useful results only for institutes with high levels of practice. A corresponding requirement in a standard increases the dispersion of results. Therefore sampling spikes were used as quality criteria only.
- Depending on the gas cleaning measures of a plant, the ducts and the locations of the measurement parts the distribution of PCDD/F-concentrations in the cross-section may be very inhomogenous. Therefore sampling at several points in the cross-section can be necessary. In a first step the sampling points in the cross-section may be chosen analogous to the rules for dust measurement.
- Taking into account the low level of participation of several sampling teams and analytical institutes in Europe the dispersion of the PCDD/F-measurement results is considerable. Nevertheless it is possible to control a limit value of 0.1 ng I-TEQ/m<sup>3</sup>.

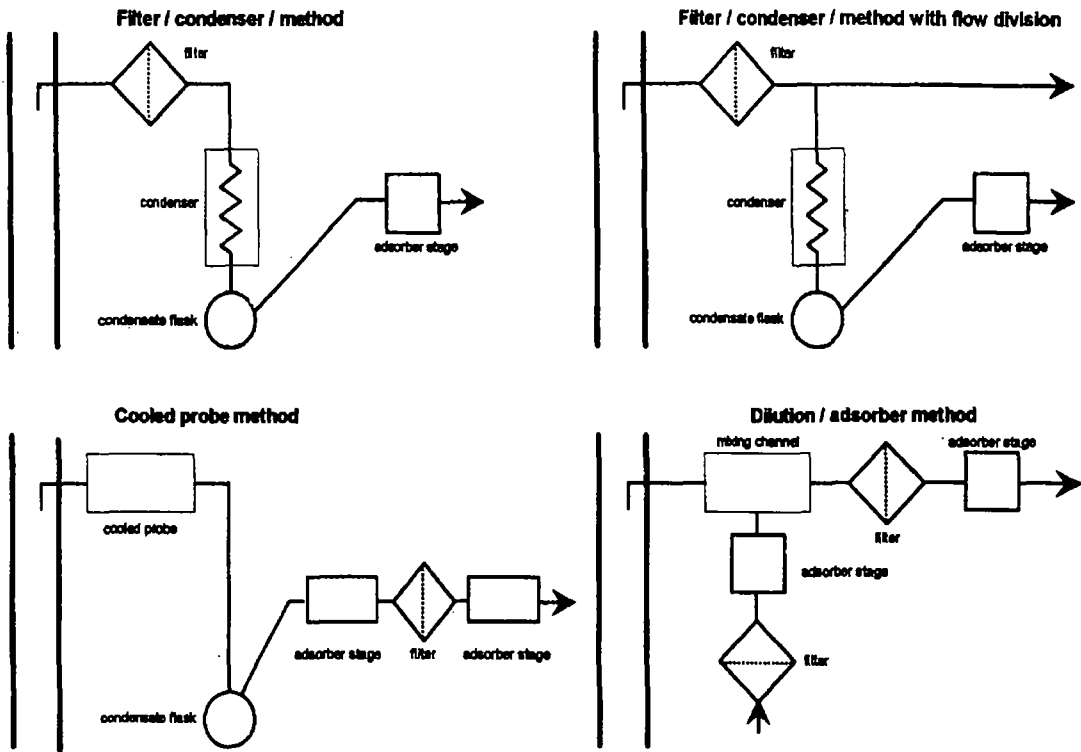


Fig. 1 : Schematic representation of the sampling system

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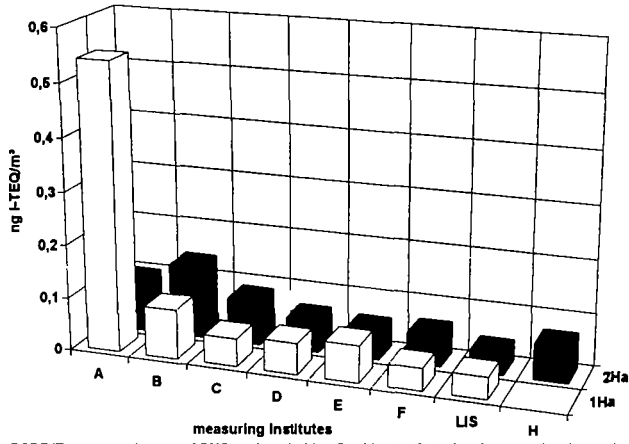


Figure 2: PCDD/F-concentrations at a MWC equipped with a fixed bed activated carbon gas cleaning system on the 1. day (1Ha) and the 2. day (2Ha); concentrations determined by different measuring institutes with different sampling systems

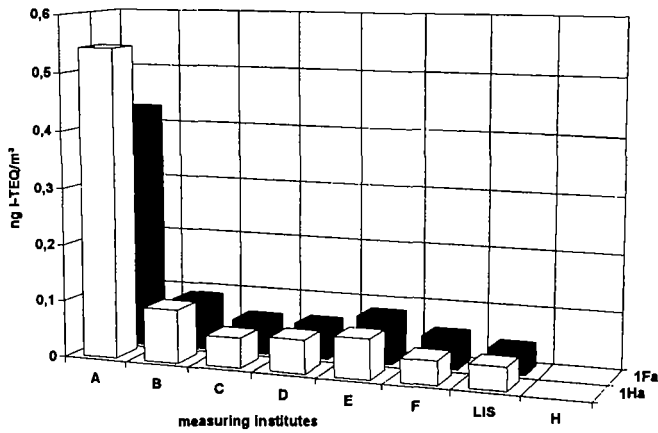


Figure 3: PCDD/F-concentrations at a MWC (fixed bed activated carbon gas cleaning system); concentrations determined by different institutes (A,B,...H) with different sampling systems and two different analytical institutes (1Ha, 1Fa)