

(special session PCDD/F gas monitors for combustion systems)

## QUICK EVALUATION OF LONG TERM MONITORING SAMPLES AND THE UNCERTAINTY OF THE RESULTS

Werner Tirler<sup>1</sup>, Massimo Donegà<sup>1</sup>, Giulio Voto<sup>1</sup>, Gerhard Kahr<sup>2</sup>

1 Eco-Center, Via Lungo Isarco sx 57, I-39100 Bolzano, Italy

2 MonitoringSystems GmbH, A-2542 Kottlingbrunn, Schloss 2, Austria

### Introduction

Since publication of EN 1948<sup>1</sup> in 1996 long-term sampling equipment has been developed to a high standard, which enables to extend the measurement time up to 30 days. The operation of this equipment is controlled by a processor, the memory enables the automatic documentation of all relevant measurement parameters for further calculation of the measurement uncertainty. Since 1993 several installations of long term sampling equipment have been done. Since last year the installation of long term sampling equipment increases rapidly. Due to the increasing installations, there is an increasing need for quick analytical determination with quick determination of the uncertainty. This presentation provides a standard operating procedure and discuss the uncertainties of the method.

### Methods and Materials

The waste incinerator Bolzano is situated in one of the most famous touristic areas of Italy. The flue gas is emitted by a 50 m height stack, with a inner diameter of 2,5 m. Since this year the waste incinerator Bolzano has installed an automatic sampling system, which is suitable to monitor the dioxin emission during the complete operation time of the waste incinerator to have a complete control of the dioxin emissions. Using two probes (2500 mm and 1300 mm length) in the relatively large stack permits to take representative samples. The dioxin emission are analysed by the laboratory of the Eco-Center Bolzano. Before sampling the sampling standards are added to the dust filter. Because of long term sampling the amount of the sampling standard is adjusted with formula 1:

$$Q_{isa}^* = Q_{isa} * \frac{c_{expected}}{0,1} * \frac{V_{sample}}{10}$$

Using this formula in Bolzano with  $c_{expected} = 0,02 \text{ ng/m}^3$  and  $V_{sample} = 150 \text{ m}^3$ , the amount of sampling and extraction standards are described in table 1.

Table 1: Added sampling and extraction standard

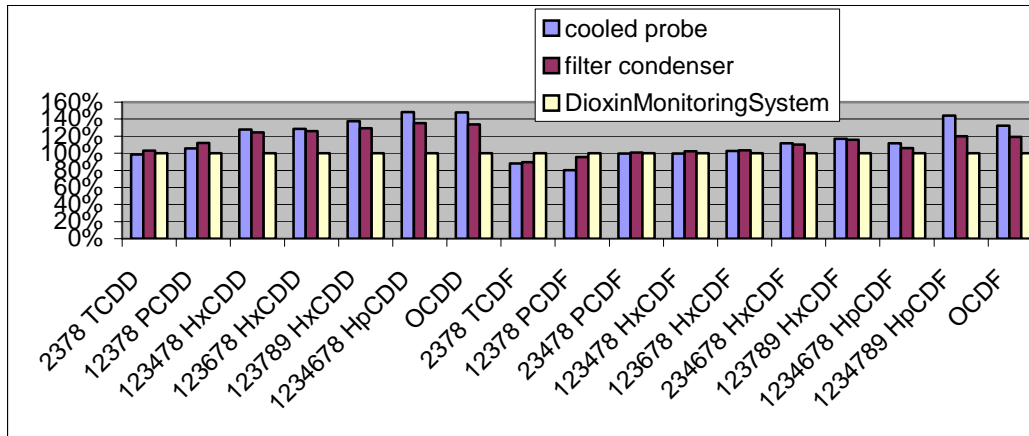
Congeners added in solution	Sampling standard
-----------------------------	-------------------

$^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDF, $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDF	each 1200 pg
$^{13}\text{C}_{12}$ -1,2,3,4,7,8,9-HpCDF	2400 pg
Congeners added in solution	Extraction standard
$^{13}\text{C}_{12}$ -2,3,7,8-TCDF ..... $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD	each 1200 pg
$^{13}\text{C}_{12}$ -1,2,3,4,6,7,8-HpCDF ... $^{13}\text{C}_{12}$ -OCDD	each 2400 pg
Congeners added in solution	Syringe standard
$^{13}\text{C}_{12}$ -1,2,3,4 TCDD, $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD	each 300 pg

The measurement is described in <sup>2</sup>. Each long term sampling is finished with a stop program, where each probe of the DioxinMonitoringSystem is heated to 300°C for 30 minutes to evaporate all of the PCDD/F and to sample them in the cartridge. This procedure reduces the sample for the laboratory to a small cartridge, which is described in <sup>3</sup>. In the laboratory the dust filter is pretreated with hydrochloric acid, extraction standard is added. Dust filter as well the PUF are extracted in a soxhlet extractor with toluene. Because there is no activated carbon in the flue gas of the incinerator, the extraction time can be reduced to 6 hours. After soxhlet extraction, a part of the extract (1/4) is used for clean up, using multilayer columns. Because of the optimised amount of extract, the clean up can be done within 2 hours. The final concentration of the sample extract is done by using a vacuum centrifuge. After the final concentration the syringe standard is added. The HRGC/HRMS evaluation is done automatically overnight

**Results and Discussion**

At the begin of the installation, comparison measurements were performed to check the representativeness of the sampling positions in the stack and to compare the time for the analysis afterwards. As comparison measurements cooled probe method and filter cooler method were used. Picture 2 shows the results:



Picture 1: isomer profiles - The toxic equivalent are in the range ±5%.

As the isomer profile in picture 1 shows, heating up of the sampling probes after the measurement is necessary in case of low temperatures in the stack to avoid losses of higher chlorinated dioxins and furans in the sampling line.

Measurements according directive 2000/76/EC show the dioxin emissions during a period of 6 to 8 hours normally not including the operation conditions during night and week end. Long time measurements covering the whole operation period of the waste incinerator. Therefore the results of the long time sampling are more representative to describe the real emissions of a waste incinerator.

Using the DioxinMonitoringSystem, optimised extraction and clean up method it is possible to have the results within 24 hours. The measurement results with its uncertainty are given with formula 2:

$$I - TEQ / m3 = \frac{m}{v} \pm \frac{1}{v^2} * \sqrt{v^2 * E_m^2 + m^2 * E_v^2}$$

$m$  ... mass of I-TEQ determined in the laboratory  
 $v$  ... volume of the sampled fluegas (dry, reference oxygen)  
 $E_m$ ... uncertainty of the determined mass of I-TEQ  
 $E_v$ ... uncertainty of the determined volume

The uncertainty of the mass of I-TEQ is defined by formula 3:

$$E_m = \sqrt{E_{fb}^2 + E_{isokin}^2 + E_{repres}^2 + E_{lab}^2 + E_{ref}^2}$$

$E_{fb}$  ... uncertainty given by field blanc  
 $E_{isokin}$ ... uncertainty for deviation to isokinetic sampling  
 $E_{repres}$ ... uncertainty of non representative sampling  
 $E_{lab}$ .... uncertainty of laboratory determination  
 $E_{ref}$ .... uncertainty of reference material

The uncertainty of the volume determination is defined by formula 4:

$$E_v = \sqrt{E_{gm}^2 + E_{pc}^2 + E_{tc}^2 + E_{hc}^2 + E_{leak}^2}$$

$E_{gm}$  .... uncertainty of gasmeter  
 $E_{pc}$  ..... uncertainty of pressure correction  
 $E_{tc}$  .....uncertainty of temperature correction  
 $E_{hc}$  ..... uncertainty of humidity correction  
 $E_{leak}$ .... Uncertainty caused by leaks

Validation of the measurement uncertainties of the used method gives the results:

	<b>Uncertainties of mass</b>	<b>±</b>
$E_{fb}$	Field blanc	±5%
$E_{isokin}$	Deviation to isokinetic sampling	±2%
$E_{rep}$	Deviation to represent. sampling	±10%
$E_{lab}$	Laboratory	±12%
$E_{ref}$	Reference standard	±10%
<b><math>E_m</math></b>		<b>±20%</b>
	<b>Uncertainties of volume</b>	<b>±</b>
$E_{gm}$	Dry gas meters	±1%
$E_{pc}$	Pressure correction	±0,5%
$E_{tc}$	Temperature correction	±1%
$E_{hc}$	Humidity correction	±2%
$E_{leak}$	Leaks	±1%
<b><math>E_v</math></b>		<b>±3%</b>

Using formula 2 with the 150 m<sup>3</sup> of sampled volume and 0,02 ng/m<sup>3</sup> concentration gives:

$$E_{tot} = \frac{1}{150^2} * \sqrt{150^2 * 0,58^2 + 3^2 * 4,5^2} = \pm 20\%$$

Using the data of the comparison measurement performed on the waste incinerator Bolzano with

$$\sqrt{E_{fb}^2 + E_{isokin}^2 + E_{rep}^2} < 5\% \quad \text{gives the results:}$$

Uncertainty of the mass     $E_m$  ..... ±16%  
 Uncertainty of the volume     $E_v$  ..... ±3%  
     **$E_{tot}$  ..... ±17%**

The results show, that the uncertainties of the dioxin results mainly are mainly dependent on the uncertainty of the reference material and the uncertainty of the laboratory. Measurements using the DioxinMonitoringSystem have uncertainties in the range of the EN1948 standard.

#### References

1. CEN/TC 264, European standard EN 1948 (1996)
2. Kahr, G Steiner, T (2001) : VDI report 1585 – Obtaining Representative Dioxin Emission Values by the Application of a Modified Fixed Installed Sampling System

3. Steiner, T, Jahr G, dioxin 2003, Long term monitoring in the frame of the new European guideline EN 1948-1.