Obtaining representative dioxin emission values by the application of a modified fixed installed sampling system

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1 Summary

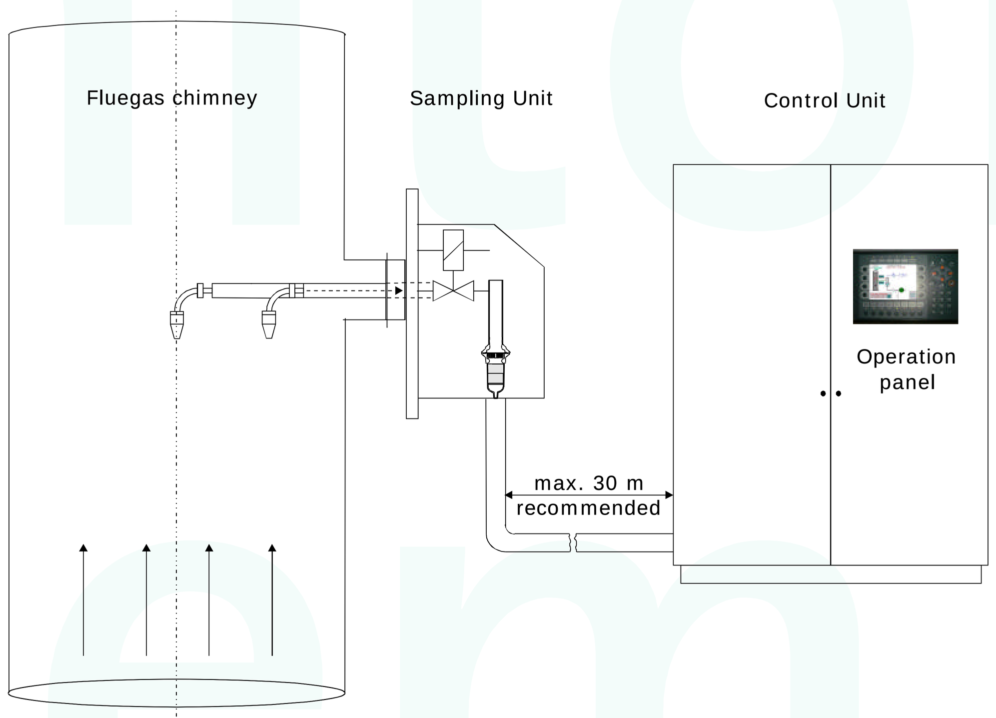
During the last 8 years numerous DioxinMonitoringSystems®, which uses the dilution method according EN 1948 part 1, were installed in the European Union. The sampling time was 8 hours as well as 7 days and 14 days.

The performance is described by the recovery rate of the sampling standard (2,3,4,7,8-P_5CDF). The mean recovery rates are 94,7 % (plant A) and 97,5 % (plant B), which are significantly higher than the results of the CEN validation tests and other literature data.
Including these excellent performance data in the calculation of the combined standard uncertainties of the toxic equivalent, the value of the combined standard uncertainty (u_{tot}) can be calculated with 24 %. Extending the measurement time to 7 days or 14 days (instead of 8 hours) u_{tot} can be reduced to 12 % and detection limits of smaller than 0.001 ng I-TE/m^3 can be obtained.

1.1 Description of DioxinMonitoringSystem®

The complete system for surveillance of 1 stack consists of the following equipment:

- one sampling unit with 2 probes
- one control unit
- filter units for delivery to the laboratory



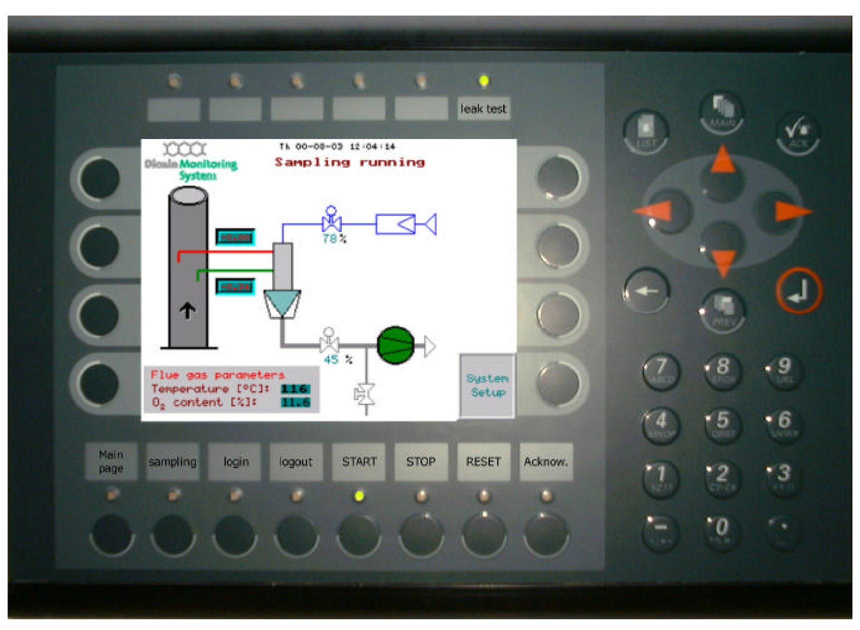
Picture 1: DioxinMonitoringSystem® schema

At stacks with inhomogen fluegas concentration, additional sampling units can be installed to ensure representative sampling.

1.2 Analyticalmethod

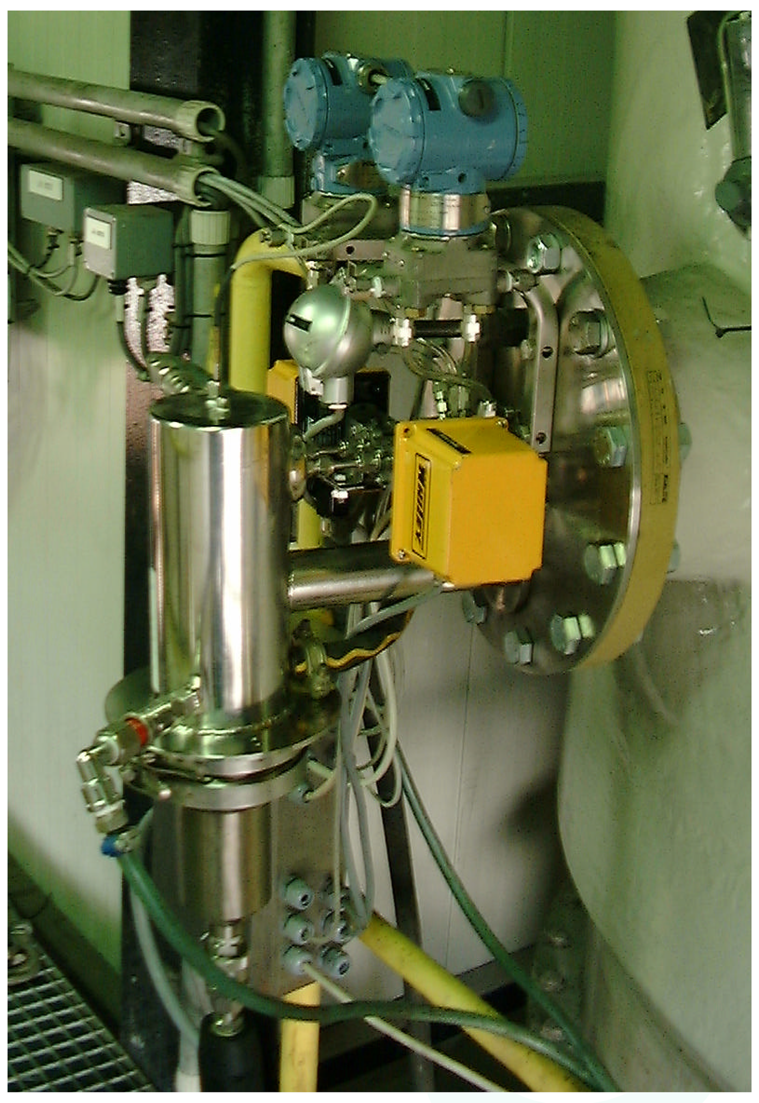
In the dioxin laboratory ^{13}C traced certified dioxin reference material (2,3,4,7,8-P_5CDF) is added to the cleaned filter unit before the sampling to check the samplings quality (recovery rate of sampling).
In the dioxin laboratory (IUTA, Duisburg) 10 ng 2,3,4,7,8-P_5CDF reference material were added to the glass fibre filter before each measurement cycle. Because of the long sampling time the amount of sampling reference material is higher than for short time monitoring. After the spikingthe mixing chamber was connected to the cartridge and sent to the plants, where this filter unit was used for the nextmeasurement of Dioxins.
Before each measurement cycle the DioxinMonitoringSystem® does an automatic cleaning process of the titanium probes to reduce blank values, as well as an automatic leak check of the complete sampling train to ensure correct volume measurement. During measurement the DioxinMonitoringSystem® works fully automatically:

- Flue gas is sampled isokinetically with two zero pressure probes at two positions of the chimney, the flow is adjusted automatically by a sensitive control valve to a probe's pressure of zero.
- To avoid condensation of water and acids, the flue gas is mixed with dry dilution air in a titanium mixing chamber. This enables dry precipitation of the dioxin in the following titanium cartridge.
- After mixing the gas flow is sucked through a titanium cartridge which has inserted a 0.1 m^2 glass fibre filter and 2 polyurethane plugs.
- Dioxins adsorbed on particles and distributed in the gaseous fraction are accumulated inside the filter unit, which consists of mixing chamber and titanium cartridge.
- A shut down of the plant is detected by defined parameters. The system pauses sampling automatically during this time (stand by mode). After restart of the plant the system continues sampling automatically.
- The oxygen signal (4-20 mA) is processed in the DioxinMonitoringSystem®. The results can be correlated to the oxygen value automatically



Picture 2: control panel

At the plant a trained engineer serves measurement's starting and stopping and also exchange of the filter units. This engineer sends this filter unit together with the measurement protocol in a transportation box to the laboratory, where the filter unit is extracted and cleaned according EN 1948 part 2 and evaluated by HRGC/HRMS according to EN1948 part 3.
During transportation and analysis of the first filter unit, an additional filter unit is available for measurements.



Picture 3: Sampling unit installed at the hazardous waste incinerator

2 Experimental

2.1 Recovery rate evaluation at two different plant types

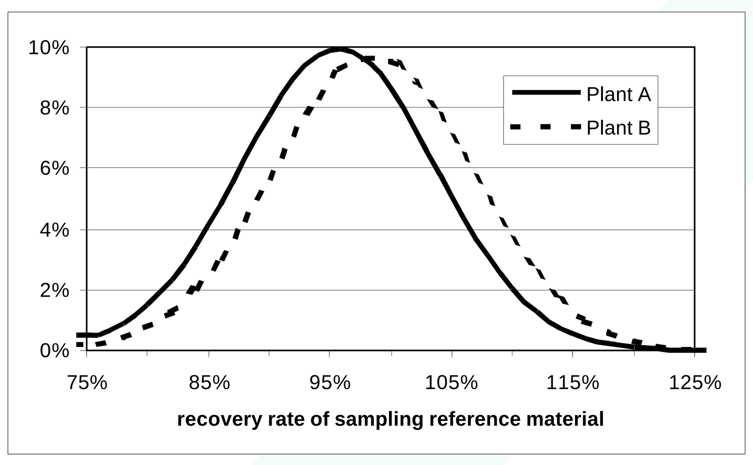
In this investigation the recovery rates for two types of incineration plants were evaluated.

Plant A

Incinerator type:	fluidised bed
Fuel:	chipboards
Dust precipitation:	bag house filter
Extended flue gas cleaning:	none

Plant B

Incinerator type:	rotary kiln
Fuel:	hazardous waste
Dust precipitation:	electrostatic precipitator
Extended flue gas cleaning:	two stage scrubbing system fixed bed activated carbon filter



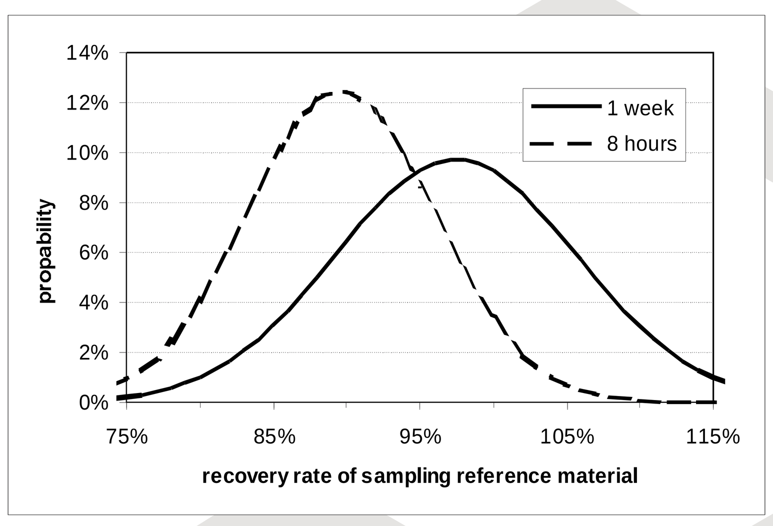
Graph 1:recovery rate at two different plants

2.2 Recovery rate evaluation with different sampling time

At standard measurement conditions the DioxinMonitoringSystem® samples flue gas for a period of one or two weeks.

At plant B short time measurements (8 hours) as well as long time measurements (1 week) were performed with the DioxinMonitoringSystem®.

As graph 2 shows, there is no significant difference between short time sampling and long time sampling.

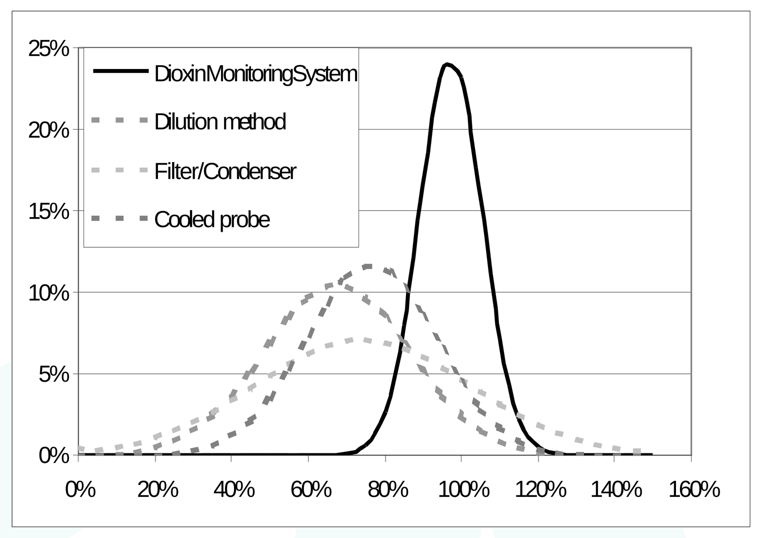


Graph 2:recovery rate at different sampling periods

3. Comparison of the results with literature data

Comparing the obtained results with the recovery rates obtained at the CEN validation measurements 1995 and the LUA comparison measurements 1995, the DioxinMonitoringSystem® - being an advanced development of the dilution method - shows

- significant higher recovery rates than the standard dilution method
- significant higher recovery rates than all standard methods



Graph 3: Comparison of recovery rates with literature data

4 Additional impacts to the estimated combined standard uncertainty

As published the combined standard uncertainty for the measurement of the I-TE is mainly dependent on:

- the application of the standard reference material (u_{srm})
- blank values induced during measurement and in the laboratory (u_{blank})
- the uncertainty of volume measurement (u_{volume})
- the deviation to representative sampling (u_{repres})
- the uncertainty defined by the sampling recovery standard ($u_{samplingtrain}$)
- inhomogen concentration profile on fly ash particles (u_{inhom})
- the incomplete coverage of the time period (u_{rs})
- the uncertainty of the recovery rate

which leads to equation 1.

$$u_{TEQ} = \sqrt{u_{srm}^2 + u_{blank}^2 + u_{volume}^2 + u_{repres}^2 + u_{inhom}^2 + u_{rs}^2 + u_{recovery}^2}$$

Equation 1: Calculation of the standard uncertainty

where

u_{TEQ}	Combined standard uncertainty of the measured toxic equivalent
u_{srm}	Standard uncertainties of the standard reference material (recovery rate)
u_{blank}	Standard uncertainty due to the impact of blank values
u_{volume}	Standard uncertainty of the volume measurement
u_{repres}	Standard uncertainty due to deviation to representative sampling
u_{inhom}	Standard uncertainty due to inhomogen dioxin concentration profile on fly ash
u_{rs}	Standard uncertainty due to incomplete coverage of the time period T_m
$u_{recovery}$	Standard uncertainty as discussed in chapter 3

5. Conclusions

Exactly defined measurement conditions, as they are adjusted with the DioxinMonitoringSystem® increase the recovery rate of the sampling reference material.

Additional long time sampling reduces the impact of blank values to the combined standard uncertainty as graph 4 shows.

Long time sampling improves also the representative sampling of particles, because the amount of sampled particles is increased by a factor of greater than 20.

Especially if particles have an inhomogen dioxin concentration profile, this effect have high impacts to the calculation of the estimated standard uncertainty.

Table 1 shows the estimated combined standard uncertainty of the dioxin measurement, obtained with the DioxinMonitoringSystem® as a function of the measurement time.

	1 week	**8 hours**
	monitoring period	
Application of the standard reference material	5 %	5 %
Blank values (measurement & laboratory)	1 %	**15 %**
Volume measurement	5 %	5 %
Deviation to representative particle sampling	5 %	**15 %**
Defined by the recovery of internal standard	9 %	8 %
u_{total}	**12 %**	**24 %**

Table 1: Uncertantie overview

Because of improved representative sampling and reduced impact of blank values, obtained with 1 week measurement period, the combined standard uncertainty (sum of all measurement impacts) can be reduced to 12 %, whichis the first acceptable value to compare results.

6 References

[1] Kube, Christine: analytical reports, IUTA, Duisburg, 1999 to 2001
[2] CEN TC 264/WG1: dioxin validation measurement, August 1995
[3] Broeker Günter: validation of three sampling trains, research report number 10402178, October 1995