Obtaining Dioxin values with low uncertainty using automatic long-term-sampling equipment and data evaluation

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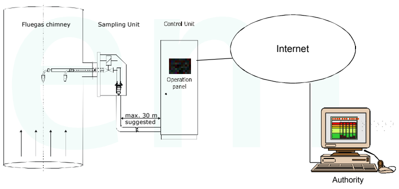
1 Summary

Since publication of EN 1948[1] 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, thememory enables the automatic documentation of all relevant measurement parameters for further calculation of the measurement uncertainty. In 2001 the authors described relevant parameters with their impact to measurements uncertainty[2]. The parameters with highest impact to uncertainty are representative dust sampling and the volume measurement (dry, O_2 corrected). At the moment the uncertainty is estimated as a sum, without individual calculation of the impact parameters.

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
- 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 a nd acids, the flue gas is mixed with dry dilution air in a titanium mixing chamber. This avoids condensation and enables dry precipitation of the dioxin in the following titanium cartridge.
- Aftermixing the gas flow is sucked through a titanium cartridgewhichhas 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 thesystem continues sampling automatically.
- TheDioxinMonitoringSystem has its own humidity measurement®. The oxigen signal is processed in the system.
- Grap1:



1.2 Experimental

In 2001 a research project was started, which included the recording, the storage, the visualisation and evaluation of all relevant parameters, which have impact to the uncertainty of representative dust sampling. These parameters are extracted online via Internet connection using TCP/IP protocol and are evaluated using Microsoft EXCEL data sheets. To improve the accuracy of the volume measurement, the periodic calibration was included as automatic process. To improve the accuracy of the correction to dry conditions a continuous calibrated humidity measurement was developed.

For legal security the system performs the measurement strictly according to EN 1948, fulfilling the following requirements:

6.1 a) The sampling train shall use a filter with a minimum retention efficiency of 99,5 % for a test aerosol with a maximum abundance at a particle diameter diameter of 0,3 µm. The filter is upstream of the sampling train (case dilution method)

6.1 b) An adsorption stage (solid adsorbent PU, XAD-2) is part of the sampling train with a minimum adsorption efficiency of 90% for the gaseous PCDDs/PCDFs (that are filter passing PCDDs/PCDFs)

6.2 h) A leak test has to be carried out before and after every sampling procedure.

6.2 i) The isokinetic sampling shall be carried out according to ISO 9096

6.2 j) Sampling shall be carried out at representative positions in the duct

6.2 l) The recovery rate of each sampling standard shall be greater than 50% calculated on the basis of the relevant extraction standard.

6.4 d) The sampling device shall contain a dilution air control adsorption stage which shall be replaced and stored after each measurement. It shall be analysed if the measurement result exceeds the limiting value. In other cases it can be discarded

All deviations to this standards or improvements to this standard has to be added(subtracted to the measurement uncertainty.

2 Impacts to the uncertainty budget

2.1 Representative sampling

At standard configuration the Dioxinmonitoringsystem samples at 2 positions in the stack with 2 calibrated 6 mm nozzles.

According to chapter 8.3.4.2. Of EN 1948 it is allowed to do the sampling at a multipoints along a single line.

This has to be reported and has to be included to the calculation of the measurement uncertainty.

The measurement uncertainty of reprepresentative sampling is evaluated beforethe installation and is mainly dependent on the type of plant . the type of fluegas cleaning system and the measurement position in the stack.

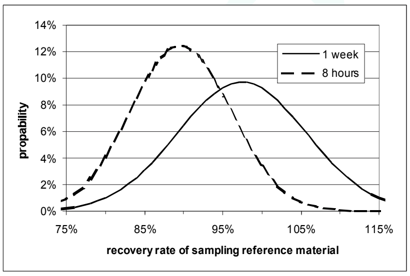
2.2 Recovery rate evaluation with different sampling time and at higher dioxin concentrations

At standard measurement conditions, the DioxinMonitoringSystem® samples flue gas for a period of 1 week to 2 weeks. It is also possible to sample 6 (8) hours with the DioxinMonitoringSystem to produce 6 (8) hour mean values as described in the European guideline 2000/76/EG

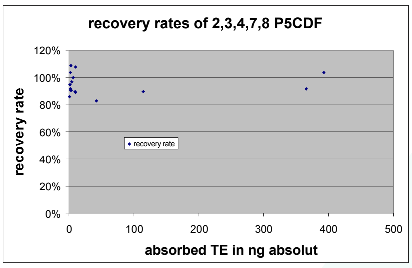
As graph 2 shows, the recovery rate (also for long time sampling) is within the range of EN 1948 part 1 (target value 50 to 100%).
The influence of high dioxin concentrations to the recovery of the recovery standard was shown in graph 3.

As this graph shows the recovery rate also at high dioxin concnetrations is within the range of EN 1948 (Target value 50 to 100%

Graph 2: recovery rates as a function of sampling time)



Graph 3: recovery rates at higher dioxin concentrations



2.3 Uncertainty of the volume measurement including humidity correction

The uncertainty of the volume measurement is dependent on:

The uncertainties of the volume measurement units

The uncertainty of the humidity measurement

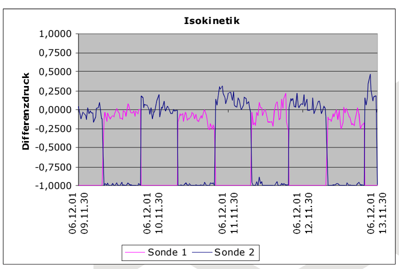
The uncertaintiy produced by leaks

The uncertainty of the volume measurement units is determined by the comparisation of both volume measurement units of the Dioxin-MonitoringSystem. The results of this comparison is documented i n the system memory.

An additional impact to the uncertainty budget is the correction to dry gas. Annex E of EN 1948 describes the measurement of the humidiy before the dioxin sampling.Especially at plants with changing humidity this method can lead to high impact to the uncertainty budget. The DioxinMonitoring-System measures the humidity of the mixed gas (in %rel) and is doing the correction for each 3 minutes mean value. The 3 minutes mean values are stored in the system

Because of the used zero pressure probes and the Dilution method thod the humidity measurement has no impact to the isokinetic adjustment.

To avaid an uncertainty impact by leaks the DioxinMonitoringSystem is doing a leak test before and after each measurement. The results of the leak test were stored in the Leak test report.



3 Impacts to the estimated combined standard uncertainty

As published [4] the combined standard uncertainty for the measurement of the I-TE by teh DioxinMonitoringSystem is mainly dependent on:

- The deviation to representative sampling
- The uncertainty defined by the sampling recovery standard ($u_{samplingtrain}$)
- The uncertainty of volume measurement (u_{volume}) including humidity correction

Other parameters like:

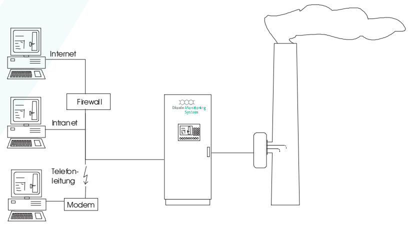
- Inhomogen concentration profile on fly ash particles (u_{inhom})
- the incomplete coverage of the time period (u_{rs})

are compensated by the use of the DioxinMonitoringSystem

This leads to the equation 1:

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

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 volumemeasurement (2.3)
- u_{repres} Standard uncertainty due to deviation to representative sampling
- u_{inhom} Standard uncertainty due to inhomogen dioxin concentration profile on fFly ash
- u_{rs} Standard uncertainty due to incomplete coverage of the time period T_m
- $u_{recovery}$ Standard uncertainty as discussed in chapter 2.2



Especially the documentation of relevant measurement parameters reduces the uncertainty of the whole measurement.

4. Conclusions

Exactly defined measurement conditions, as they are adjusted with the DioxinMonitoringSystem® lead to exactly defined and low measurements uncertainty.

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 %, which is the first acceptable value to compare results.

This is possible by the documentation of the parameters (as 3 minutes mean values) by the software of the DiocinMonitoringSystem.

5 References

[1] Kube, Christine Analytical reports IUTA, Duisburg (1999,2000,2001)
[2] CEN TC 264/WG1Dioxin validation measurement: (August 1995)
[3] Broeker Guenterr: Validation of three sampling trains Research report number 10402178 (Oktober 1995)