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

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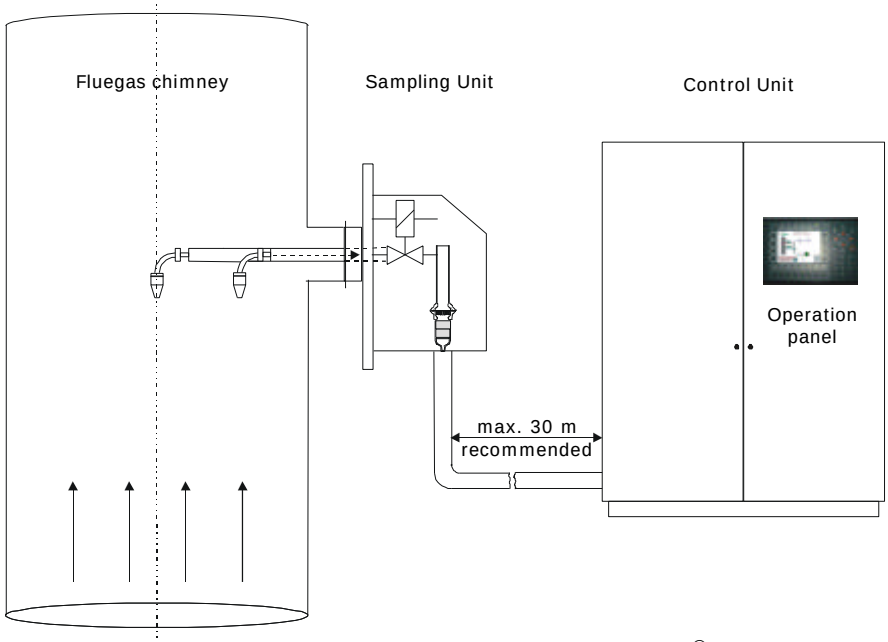
Summary

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 further be reduced to 12 % rel and detection limits of smaller than 0.001 ng I-TE/m^3 can be obtained.

1 Description of the fixed installed sampling system

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

- one sampling unit
- one control unit
- one filter unit + additional filter units (for delivery to the laboratory)



Picture 1: DioxinMonitoringSystem® schema

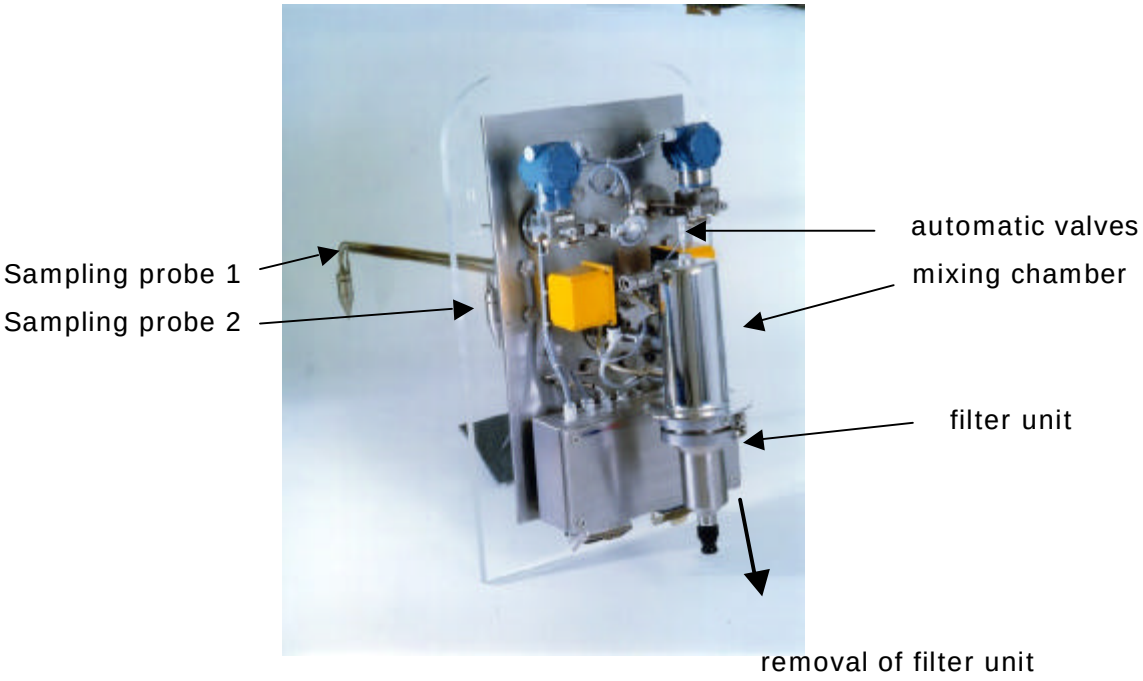
1.1 Description of the Sampling unit

The flue gas is sucked alternating by one of two heated **sampling probes**. Their material titanium ensures good resistance against corrosive flue gas components. Each of the sampling probes is designed as “zero pressure probes” to ensure isocinetic sampling. Calibrated 6 mm nozzles ensure accurate sampling of the dust fraction.

Two **automatic valves,** one for each probe, permits the selection of one of the two stack positions. Behind the valves a thermostatic **mixing chamber** made of titanium is situated, where the extracted flue gas is mixed with dried and dust free dilution air.

The **filter unit** is mounted directly to the mixing chamber. The mixed gases are sucked through the filter unit. The design of the filter unit is according EN 1948 part 1. The filter unit has a unique construction to enable long time surveillance.

The filter unit is changed at the start of a new measurement period. Because of the use of titanium the filter unit can easily be treated thermal to obtain very low blank values for next measurement cycles.



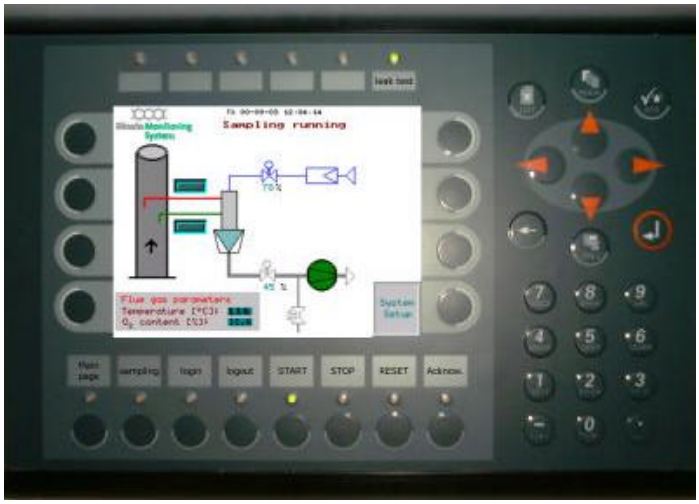
Picture 2: Sampling unit

1.2 Description of the Control unit

The control unit performs the following routines:

- start and stop of the measurement
- automatic leak test (to avoid leakage)
- automatic cleaning routine for the probes (to reduce blank values)
- automatic control of the isocinetic sampling
- automatic temperature control of mixing chamber and filter unit
- configureable stand by parameters (e.g. in case of plant shut down)
- automatic measurement reports

For comfortable operation of the measurement process the control unit is equipped with an operation panel. This panel is situated in the front door of the control unit.



Picture 3: Operation panel

1.3 Analytical method

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 sampling to check the samplings quality (recovery rate of sampling).

In the IUTA dioxin laboratory (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 addition of this reference material the mixing chamber was connected to the cartridge and sent to the plants, where this filter unit was used for the next measurement of PCDD and PCDF.

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 avoids condensation and 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 corrected to the oxygen value automatically

At the plant a trained engineer serves measurement's starting and stopping and exchange of the filter unit.

This engineer sends the 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 EN 1948 part 3.

During transportation and analysis of the first filter unit, an additional filter unit is available for measurements.

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

Fluidised bed incinerator, incinerating chipboards
Bag house dust precipitation filter

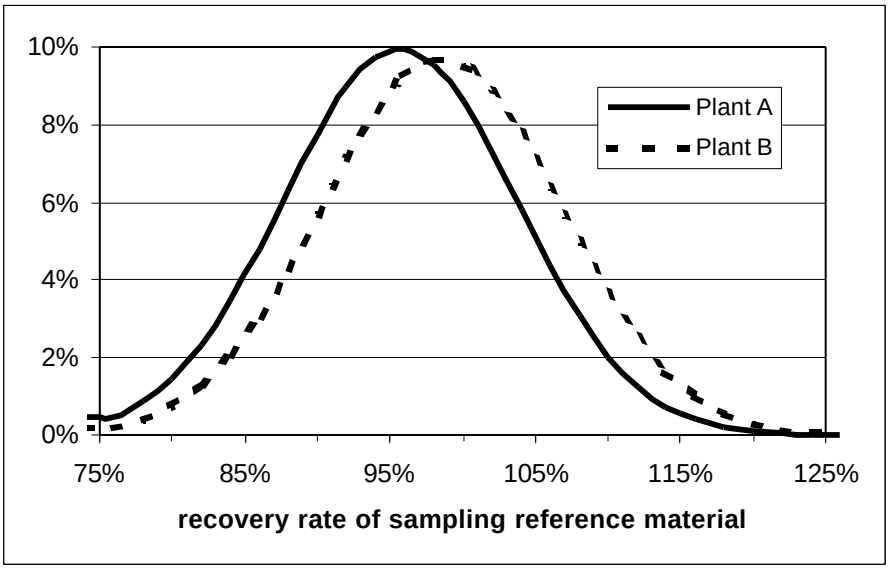
Plant B

Rotary kiln furnace incinerating hazardous waste
Electrostatic precipitator as dust precipitator
2 stage scrubbing system
Fixed bed activated carbon filter

Table 1, graph 1: Statistical evaluation of recovery rates as a function of plant type

	average recovery rate of 2,3,4,7,8 P_5CDF	expanded standard uncertainty (p = 0.95)
Plant A	94.7 %	17.0 %
Plant B	97.5 %	18.4 %

The statistical evaluation shown in table 1 is based on the evaluation of 54 samples. As table 1 shows, there is no significant difference in the average recovery rate and also no significant difference in the calculated expanded standard uncertainty.



2.2 Recovery rate evaluation with different sampling time

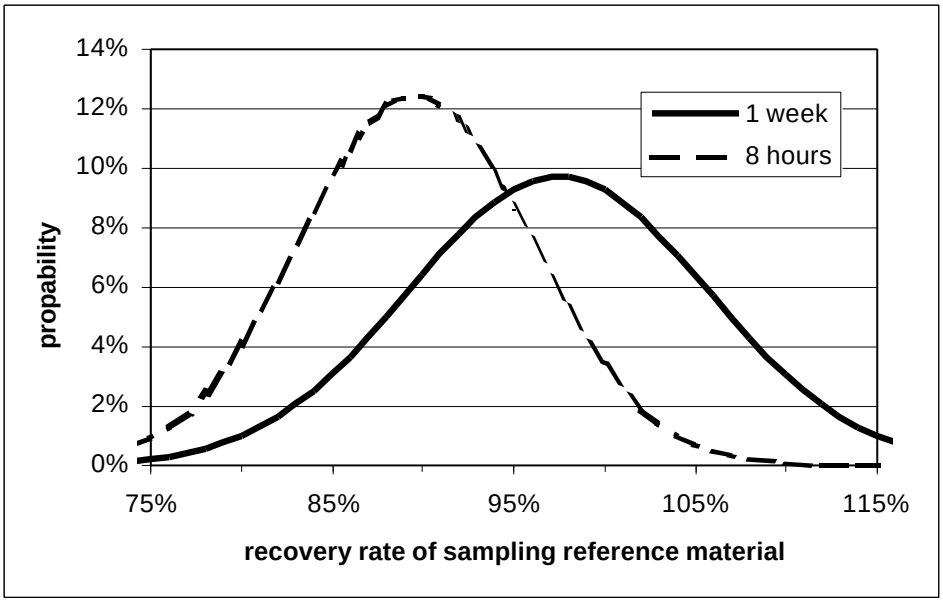
At standard measurement conditions, the DioxinMonitoringSystem® samples flue gas for a period of 1 week to 2 weeks. At plant B short time measurements (up to 8 hours) as well as long time measurements (1 week) were performed with the DioxinMonitoringSystem®.

Table 2: Statistical evaluation of recovery rates as a function of the sampling time.

	average recovery rate of 2,3,4,7,8-P_5CDF	Expanded standard uncertainty
Short time sampling (< 8 hours)	89.6 %	6.4 %
Long time sampling (1 week)	97.5 %	18.4 %

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

Graph 2:



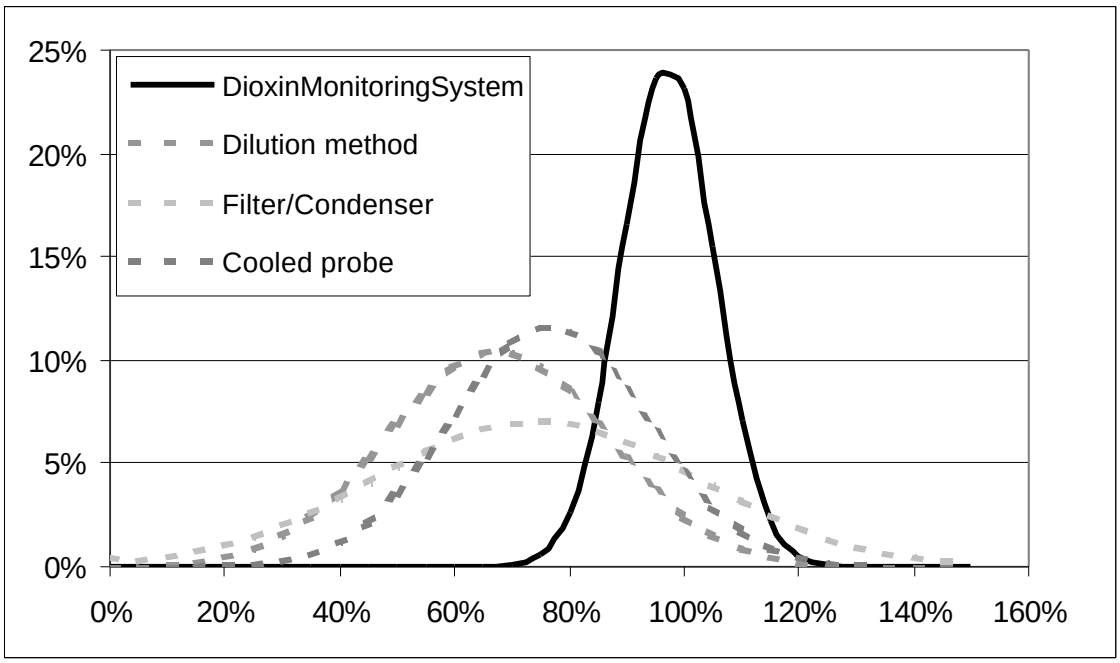
3. Comparison of the results with literature data

Comparing these 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

Table 3, graph 3: Comparison of recovery rates with literature data

	average recovery rate of 2,3,4,7,8-P_5CDF	expanded standard uncertainty (p=0.95)
Plant A		
Long time sampling (2 weeks)	**94.7 %**	17.0 %
Plant B		
Short time sampling (< 8 hours)	89.6 %	6.4 %
Long time sampling (1 week)	**97.5 %**	18.4 %
CEN Validation measurements 1995 /2/		
Dilution method	65 %	41 %
Filter condenser method	72 %	60 %
Cooled probe	74 %	37 %
LUA Report 1995 /3/		
'Messinstitut 1'	75 %	34 %
'Messinstitut 2'	88 %	58 %
'Messinstitut 3'	81 %	25 %



4. Additional impacts to the estimated combined standard uncertainty

As published [4] 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 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 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

4.1 Uncertainty of the standard reference material

The uncertainty of the standard reference material is defined by the quality assurance procedure of each dioxin laboratory.

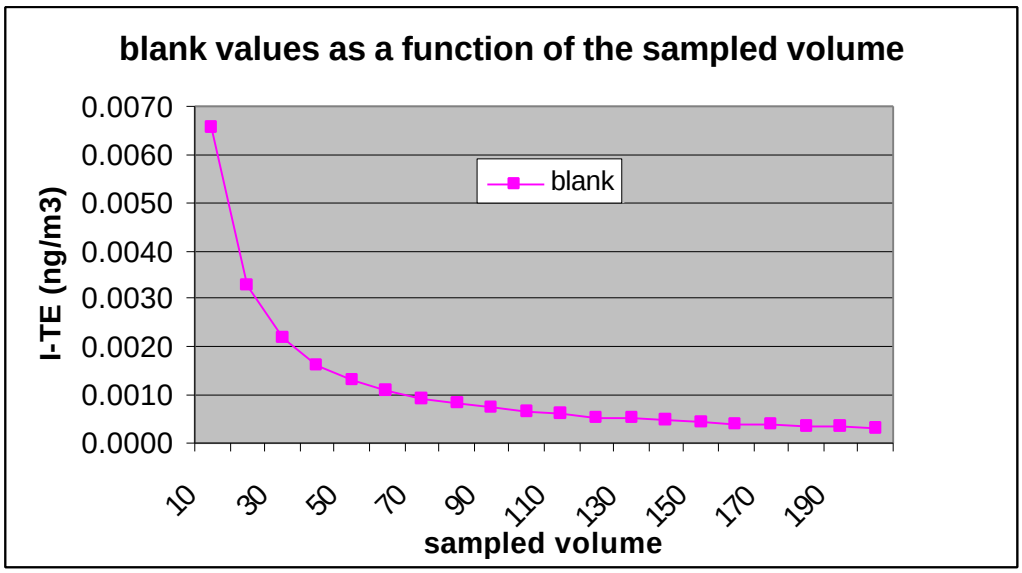
It is dependent on the defined threshold level for verification of the standard reference material and defined by the application of a control chart. A threshold level of 5% gives a standard uncertainty of ± 5 %.

4.2 Uncertainty due to blank values

During the measurement process and during extraction and clean up process in the laboratory blank values give an impact to the uncertainty.

This uncertainty can be reduced by increasing the sampled stack gas volume. As graph 4 shows, this uncertainty can be reduced to values below 0.0005 ng/m3.

graph 4



4.3 Uncertainty of volume measurement

This uncertainty is dependent on:

- the uncertainty of the gasometers
- the uncertainty of the temperature measurement
- the uncertainty of the pressure measurement

Because of the use of two volume measurement devices, a unique feature of the dilution method, the uncertainty of the volume measurement can be checked by comparing both volume measurements. The DioxinMonitoringSystem® does the comparison periodically

during each measurement cycle, comparing the volume measurement device 1 with the volume measurement device 2.

By applying a threshold value of 1% (control card of periodical check), the uncertainty is given with $\pm$ 5 %.

4.4 Deviation to representative particle sampling

Dependent on the temperature in the stack and the character of the particles, a portion of the dioxins is adsorbed on the particles. Therefore representative particle sampling is essential. Representative particle sampling is dependent on:

- deviation to isokinetic sampling
- number of probes in the stack
- amount of particles sampled with the filter unit

The uncertainty caused by the deviation to "representative particle sampling" can be reduced by

- use of zero pressure probes
- use of a high number of probes in the stack
- increase of the sampled dust fraction

At each sampling location a zero pressure probe measure the difference pressure between sucked flue gas and the flue gas in the stack. This method ensures lowest deviations to isokinetic sampling. The difference pressure (of the zero pressure probes) is adjusted to 0.03 mbar and is monitored as trend for each probe.

Two probes for extraction of the flue gas are connected with the sampling unit. Cumulative sampling at both stack positions is done. Every 60 minutes the valves switch to the other probe.

To increase the amount of sampled particles the measurement time is increased to 7 days (14 days) by the DioxinMonitoringSystem®. This results in a decrease of the uncertainty $u_{representaive}$.

Dependent on the type of flue gas cleaning system, the emitted particles can have different surface and different adsorption capacity. Therefore repeated dioxin analysis of flyash samples give scattered dioxin values, dependent on the inhomogenity of the fly ash.

The DioxinMonitoringSystem® samples a high amount of particles on the surface of a particle filter as dry particles.

In the dioxin laboratory before analysis visual inspection of the particle filter allows to compare the precipitated fly ash with previous samples and to estimate the uncertainty caused by inhomogenity.

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

Table 5:

	8 hours measurement	1 week measurement
u_{srm}	5 %	5 %
u_{blank}	15 %	1 %
$u_{volume\ measurement}$	5 %	5 %
$u_{representative}$	15 %	5 %
$u_{recovery\ rate}$	8 %	9 %
u_{total}	**24 %**	**12 %**

valid for flue gas samples with homogen dioxin concentration profile

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.

6. References

/1/ Kube, Christine Analytical reports IUTA, Duisburg (1999, 2000, 2001)
/2/ CEN TC 264/WG 1 Dioxin Validation Measurements (August 1995)
/3/ Bröker, Günter Validation of three sampling trains
Research report No. 104 02 178 (Oktober 1995)