USING CONTINUOUS DIOXIN MEASUREMENT IN THE FRAME OF THE EUROPEAN LEGISLATION

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Introduction

Continuous dioxin measurement is done since 1993 on several plants in Europe. Air emission measurement for dioxins are defined the council directive 2000/76/EC, the details of the measurement are defined in the EN 1948 standard

Council directive 2000/76/EC defines in Annex V (d) the legal limit value and in Annex I the equivalence factors. Annex III defines, that all measurements have to be done as given by CEN standards, which is in the case of dioxin measurement the EN 1948 standard.

Part 1 describes the sampling, part 2 and 3 describes the analytical determination the laboratory. EN 1948 part 1 allows to use three methods: filter/cooler method, dilution method and cooled probe method.

Part 4, now developed by CEN/TC 264/WG 1, includes the measurement of the "dioxinlike" PCBs to the measurement.

Continuous monitoring extends the sampling period from 6/8 hour measurement to 1 week (2 week), which enables complete surveillance of the municipal waste incinerator operation time. So the total dioxin emission (I-TEQ as well as WHO-TEQ) of the waste incinerator can calculated, which allows to calculated the specific impact of this plant to the food chain.

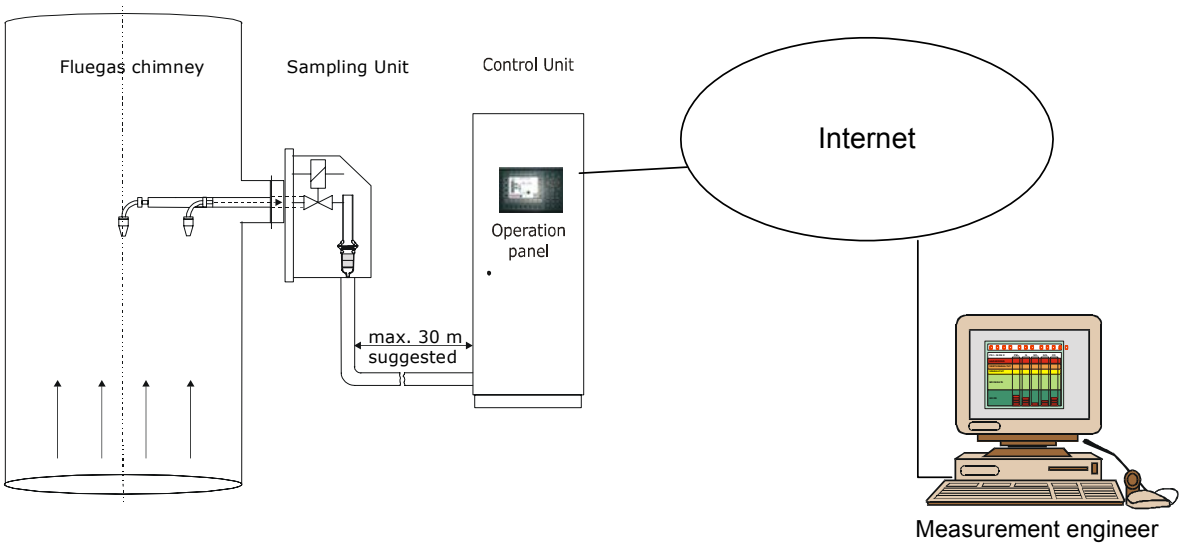
There are some important reasons, why to check the emissions of toxic dioxins and PCBs more frequently and in a continuous way and to include also the "dioxinlike" PCBs:

- **Bioaccumulation of PCDD/Fs and PCBs is continuing along the trophic chain**
  One starting point of the trophic chain is air
- **Toxic properties of PCDD/Fs and PCBs seem to be underestimated**
  As a consequence, WHO developed new assessment of the toxic equivalency of PCDD/Fs and PCBs. The new assessment leads to changes of up to 40% of the equivalency values, which are calculated from the measured concentrations of PCDD/Fs and PCBs.
- **Impact of some plants to the food chain seems to be underestimated**
  Measurements once a year can not check problems of the flue gas cleaning system, if efficiency for dioxin removal changes

Description of the automatic measurement system

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

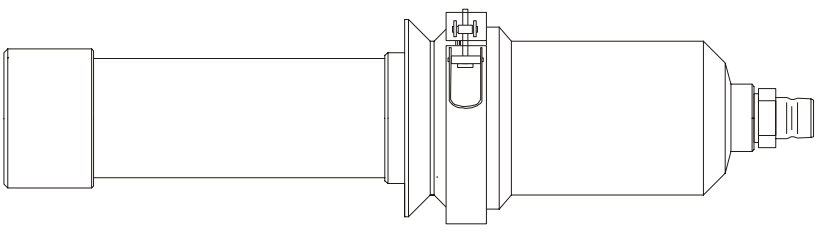
At the plant the process engineer serves measurement's starting and stopping and exchange of the filter unit. The DioxinMonitoringSystem® is operated with 8 hours and 7 days, 14 days or monthly sampling time and delivers the I-TEQ mean value of the measurement period.
The DioxinMonitoringSystem® performs the following routines automatically during measurement:

- automatic leak test (to avoid leakage) before start
- automatic cleaning routine for the probes (to reduce blank values) before start
- automatic control of the isokinetic sampling
- automatic switching between the two probes in a 30 minutes cycle
- automatic temperature control of mixing chamber and filter unit
- configurable stand by parameters for automatic stop during of plant shut down and automatic restart
- automatic measurement reports

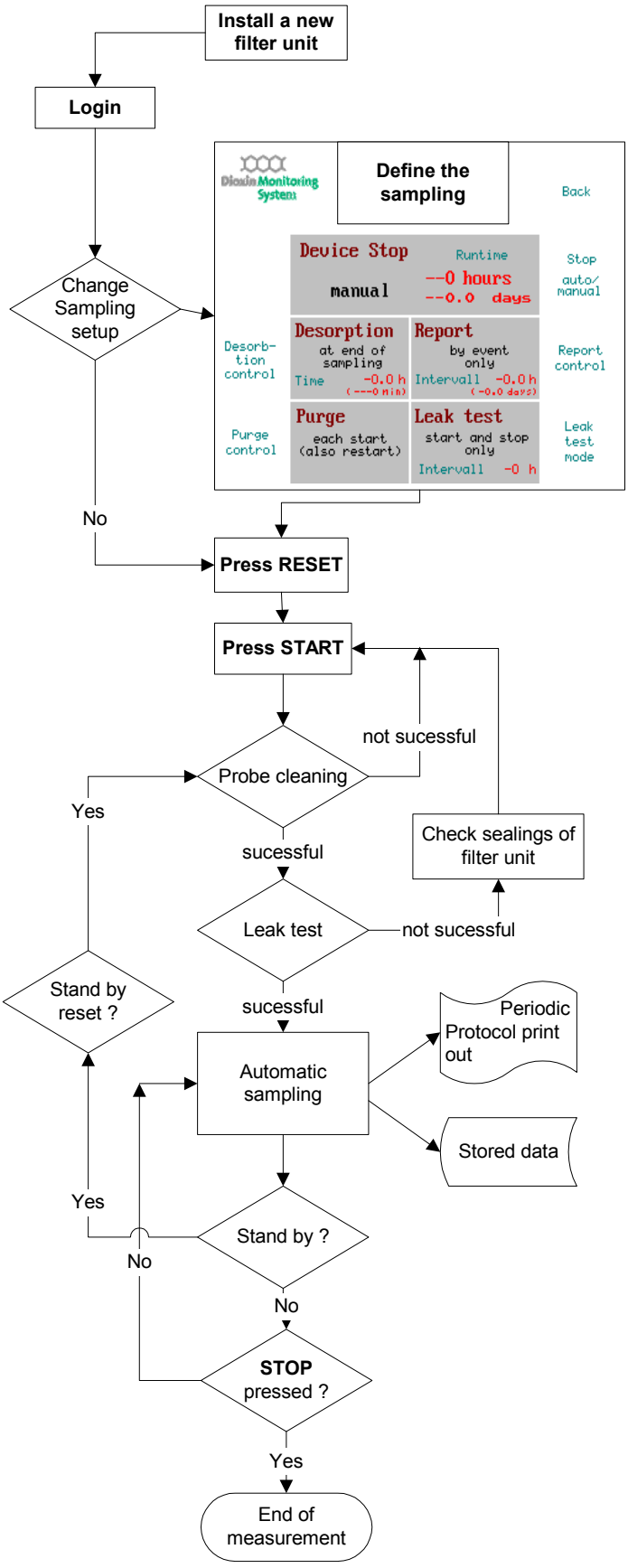
After stopping the measurement the engineer sends the filter unit with connected mixing chamber together with the measurement protocol in a transportation box to the laboratory, where the filter unit is extracted and cleaned according EN 1948 part 2 and evaluated by HRGC/HRMS according to EN 1948 part 3.

The engineer receives the results by E-mail from the laboratory, including

- ❑ the I-TEQ values obtained at the laboratory
- ❑ the statistical evaluation of the obtained results



Picture 1: filter cartridge (filter chamber + mixing chamber)



Picture 3: Overal schema of the automatic measurement

Description of the laboratory procedure
The filter cartridge is to be prepared by the analysing laboratory. The laboratory cleans the cartridge, inserts filter and adsorbent and adds the sampling standards: The amount of sampling standard is adjusted to the expected concentration range and the expected volume of sampling. Afterwards the cartridges are sent to the plant, where the measurement engineer inserts the cartridge and starts the measurement.

After receiving the cartridges back from plant, the cartridges can be stored at room temperature. The dust filter of the cartridge is treated with 1 ml concentrated hydrochloric acid. The adsorbent (Polyurethan foam) and the treated filter are transferred into a Soxhlet extractor. The extraction standard is added. Depended on the concentration range, the amount of extraction standard is adjusted accordingly:

- amount according EN 1948-2 for up to 20 m^3 of sampled flue gas and also to check for very low concentrations (0,0001 to 0,005 ng I-TEQ/m^3
- amount 10 times higher for weekly or biweekly sampling in the range of 0,01 to 0,2 ng I-TEQ/m^3
- amount 20 times higher for monthly sampling period in the range of 0,01 to 0,2 ng I-TEQ/m^3

The Clean up is done by using the methods EN 1948-2 and prEN 1948-4 to separate PCDD/Fs and toxic PCBs. The cleaned extracts are analysed using HRGC/HRMS. In case of long term sampling, it is possible to adjust the amount of final extract in the range of 10 µl to 200 µl dependent on the concentration in the sample.

The cartridges are extracted according EN 1948 part 2. Extracts are cleaned up according EN 1948 part 2 and 4. Concentrated and cleaned extracts are analysed according EN 1948 part 2 and 4. Evaluation and multiplying with the individual I-TEY factors gives the results for I-$TEQ_{PCDD/F}$ and I-TEQ_{PCB}. Summing up both results gives the I-TEQ_{WHO}.

Congener	Concentration ng/m^3 (dry, 11% O_2)	
2,3,7,8 T_4CDD	0,0011	
1,2,3,7,8 P_5CDD	0,00204	
1,2,3,4,7,8 H_xCDD	0,0012	
1,2,3,6,7,8 H_xCDD	0,00214	
1,2,3,7,8,9 H_xCDD	0,0013	
1,2,3,4,6,7,8 H_pCDD	0,01239	
OCDD	0,02482	
2,3,7,8 TCDF	0,03816	
1,2,3,7,8 P_5CDF	0,06634	
2,3,4,7,8 P_5CDF	0,02257	
1,2,3,4,7,8 H_xCDF	0,02009	
1,2,3,6,7,8 H_xCDF	0,02504	
2,3,4,6,7,8 H_xCDF	0,01546	
1,2,3,7,8,9 H_xCDF	0,00270	
1,2,3,4,6,7,8 H_pCDF	0,03830	
1,2,3,4,7,8,9 H_pCDF	0,00216	
OCDF	0,00736	
I-TEQ		0,027 ng I-TEQ/m^3

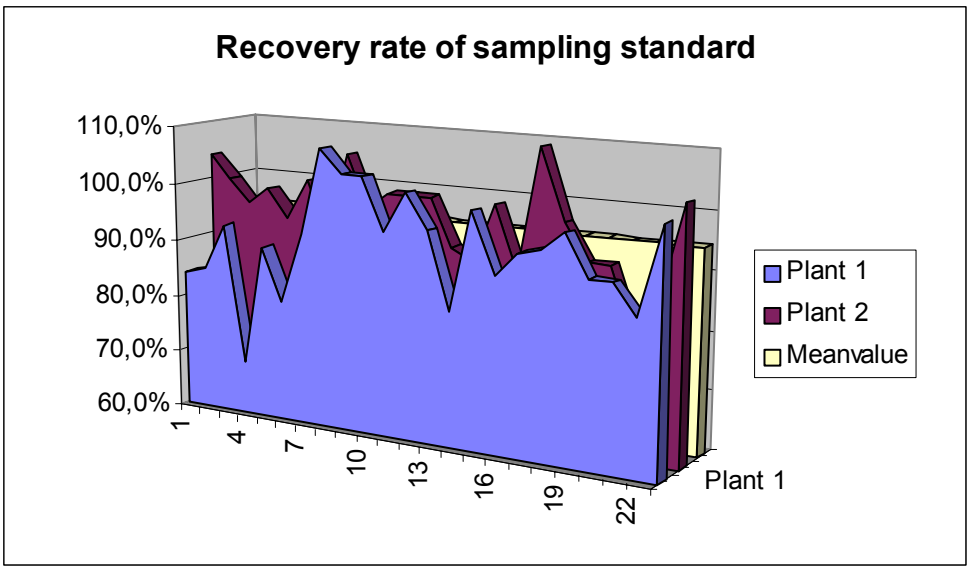
Congener	Concentration ng/m^3 (dry, 11% O_2)	
PCB 77	0,034	
PCB 81	0,004	
PCB 123	0,010	
PCB 118	0,162	
PCB 114	0,005	
PCB 105	0,044	
PCB 126	0,010	
PCB 167	0,027	
PCB 156	0,032	
PCB 157	0,009	
PCB 169	0,003	
PCB 189	0,015	
		0,0011 ng I-TEQ$_{PCB}$/m^3

Validation data of the Long term sampling
In EN 1948-1:200x the method validation criteria are described in chapter 7.1. According these requirements, Long term sampling exactly done according EN 1948, needs further validation of:

1. Sufficient sample shall be collected during the validation trial so that the detection limit is less than 5% of the total amount collected (expressed in I-TEQ)
2. The original sampling train and the additional adsorbtion stage shall be analysed separately. More than 90% of the total I-TEQ shall be found in the original sampling train
3. The mean adsorber temperature during method validation should not be exceeded in the sampling campaign without further validation at the higher temperature

Method validation criteria 1 is not important for long term sampling, because the sampled volume is much more higher than by a 6 hours measurement.

Criteria 2 can easily checked by evaluation of the recovery rate for a series of measurements and calculating the mean value of sampling standard recovery.



Picture 4: Validation data of the recovery standard for biweekly sampling period

As Picture 4 shows, the mean value of the recovery rate for the sampling standards is 94,7 %, no value is below 65%. The minimum requirement of EN 1948 is fulfilled with a high extend.

To evaluate criteria 3, three adsorber temperatures were validated: 40°C, 50°C and 60°C with a volume of 500 m^3 (flue gas + dilution air).

Congener	Part at 1st adsorber at 40°C	Part at 1 st adsorber at 50°C	Part at 1 st adsorber at 60°C
2,3,7,8 T_4CDD	100,0%	99,1%	96,2%
1,2,3,7,8 P_5CDD	100,0%	100,0%	100,0%
1,2,3,4,6,7,8 H_pCDD	100,0%	98,3%	98,0%
OCDD	100,0%	98,6%	98,7%

The criteria recovery>90% is fulfilled even at 60°C adsorber temperature.

Conclusions

Due to its flexibility and high recovery of the sampling standards, the DioxinMonitoringSystem is able to extend the sampling time to 4 weeks.

With monthly (or biweekly) sampling period it is able check the well function of the flue gas cleaning system, so that the period of possible exceedings of the legal limit 0,1 ng I-TEQ will be reduced to a minimum.

Long term sampling allows also to measurements very low concentrations of dioxin emissions. It is possible to achieve detection limits of 0,0001 ng I-TEQ/m^3.

Continuous monitoring of dioxin emissions avoids underestimation of the real emitted dioxin emissions and checks the impact to the trophic chain in the same way as for the other pollutants like SO_2, CO. Gaps in knowledge will be reduced in an effective way by checking the sources.

With the same measurement system it is possible to determine I-$TEQ_{PCDD/F}$ and I-TEQ_{PCB}.

Therefore the use of continuous dioxin monitoring will support the compliance with EU Directive 94/67/EC of 16 December 1994 on the incineration of hazardous waste and of EU Directive 2000/76/EC of 4 December 2000 on the incineration of waste by checking the legal limit values in a quasi continuous way. The emissions of toxic dioxins and also of toxic PCBs will be reduced effectively.

References:

1. EN-1948-1:1997, Stationary source emissions – Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs – Part 1: Sampling
2. prEN 1948-4:200x, Stationary source emissions – Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs – Part 4: Sampling and analysis of dioxin-like PCBs
3. G. Kahr, Quality assurance of the dioxin precipitation at a hazardous waste incinerator in the Netherlands using permanent dioxin monitoring, CEM 2001