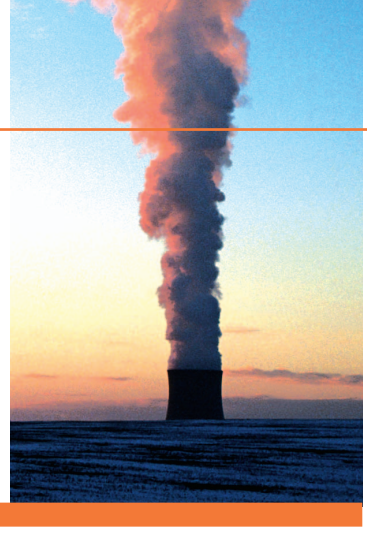

Using Continuous Dioxin Measurement

WITHIN THE FRAMEWORK OF THE EUROPEAN LEGISLATION

Author Details

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Continuous dioxin measurement has been carried out since 1993 on several plants in Europe. Air emission measurement for dioxins are defined by 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 carried out as stated by CEN standards, which in the case of dioxin measurement the EN 1948 standard.

Part 1 describes the sampling, part 2 and 3 describe the analytical determination by the laboratory. EN 1948 part 1 allows the use of 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 "dioxin like" 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 be calculated, which allows the calculation of the specific impact of this plant to the food chain.

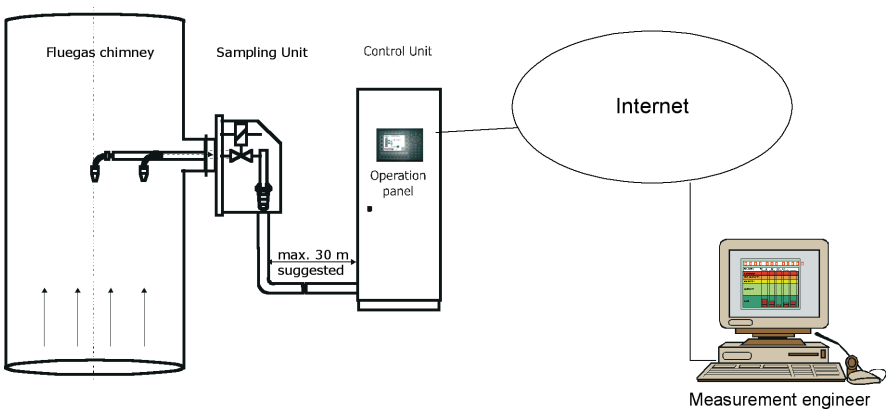
There are some important reasons why to check the emissions of toxic dioxins and PCBs more frequently in a 'continuous way' and to include the "dioxin like" PCBs:

- **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 operating plants to the food chain seem to be underestimated.** Measurements once a year cannot check problems of the flue gas cleaning system, if efficiency for dioxin removal changes

Description of an 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® schematic

At the plant the process engineer controls the measurement cycle start and stop period and exchange of the filter unit. The DioxinMonitoringSystem® can operate for 8 hours, 7 or 14 days or monthly sampling period and delivers the I-TEQ mean value of the total measurement period.

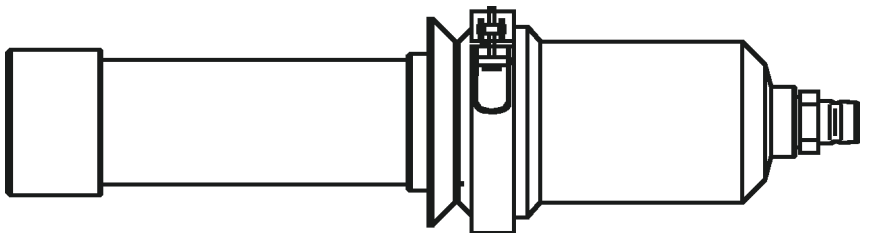
The DioxinMonitoringSystem® performs the following routines automatically during the measurement period:

- automatic leak test (to avoid system leak) before start up
- 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 plant shut down and automatic restart
- automatic measurement reports

After stopping the measurement cycle, the engineer sends the filter unit along with the connected mixing chamber and with the measurement protocol in a transportation box to the laboratory, where the filter unit is extracted and cleaned according to 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 2: filter cartridge (filter chamber + mixing chamber)

Description of the laboratory procedure

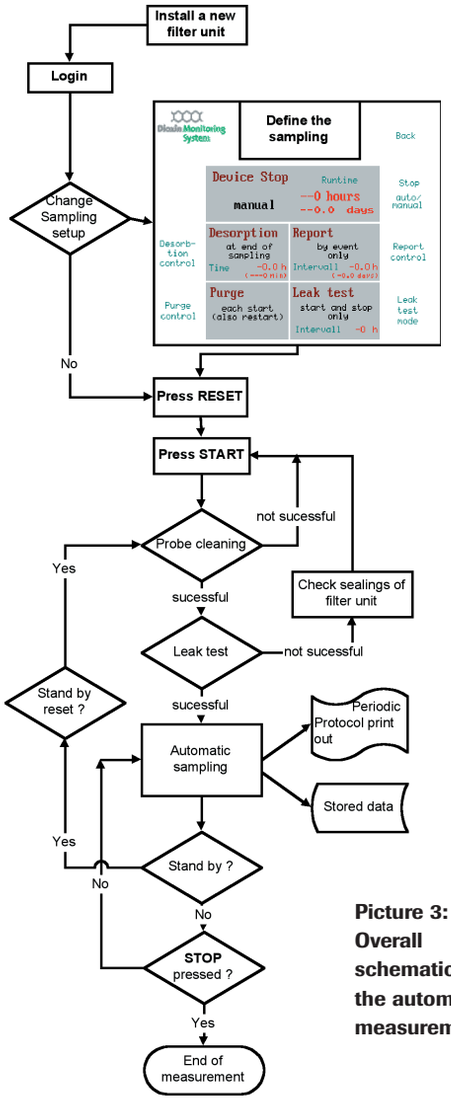
The filter cartridge is prepared by the analysing laboratory. The laboratory cleans the cartridge, inserts filter and adsorbent and adds the sampling standards: The amount of sampling standard is adjusted to the expected concentration range and the expected volume of sampling. Afterwards the cartridges 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 1ml concentrated hydrochloric acid. The adsorbent (Polyurethane 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' recovery follows 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 $I\text{-}TEQ_{PCDD/F}$ and $I\text{-}TEQ_{PCB}$. Summing up both results gives the $I\text{-}TEQ_{WHO}$.



Picture 3: Overall schematic of the automatic measurement

Congener	Concentration ng/m³ (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/m³**
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$_{PCB}$/m³

Validation Data for Long Term Sampling

In EN 1948-1:200x the method validation criteria are described in chapter 7.1.
According to these requirements, long term sampling performed exactly to 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 are not important for long term sampling, because the sampled volume is much greater than a 6 hour measurement.

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

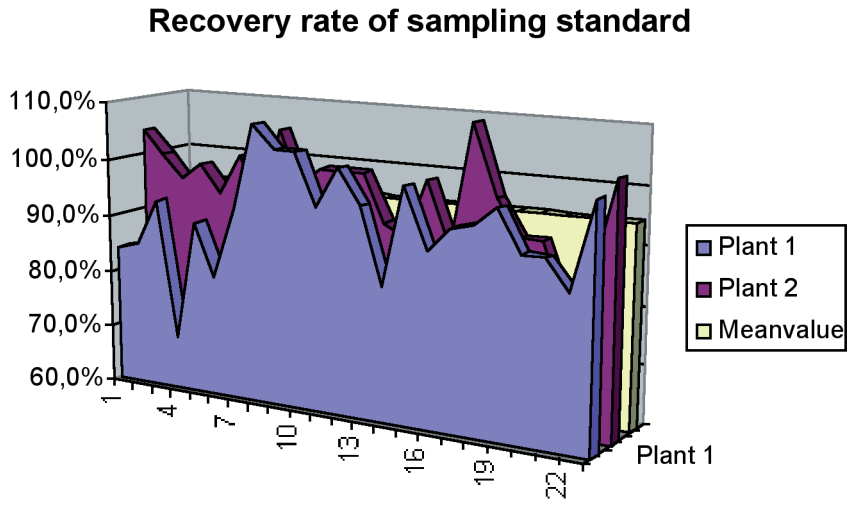
As Picture 4 shows, the mean value of the recovery rate for the sampling standards is 94,7 %, no value is below 65%. The minimum requirement of EN 1948 is fulfilled with a high extend.

To evaluate criteria 3, three adsorber temperatures were validated: 40°C, 50°C and 60°C with a volume of 500 m³ (flue gas + dilution air). The criteria recovery>90% is fulfilled even at 60°C adsorber temperature.

Congener	Part at 1st Adsorber at 40°C	Part at 1st Adsorber at 50°C	Part at 1st 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%

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



Picture 4: Validation data of the recovery standard for bi-weekly sampling period

Conclusions

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

With monthly (or biweekly) sampling period it is possible to check and monitor the function of the flue gas cleaning system, so that the period of possible exceedances of the legal limit 0,1ng I-TEQ will be reduced to a minimum. Long term sampling also allows measurements to very low concentrations of dioxin emissions. It is possible to achieve detection limits of 0,0001ng I-TEQ/m³. 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 of the 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.