INNOVATIONS IN PERMANENT MONITORING OF PCDD/PCDF FROM A HAZARDOUS WASTE INCINERATOR

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1. Introduction

Since PCDD/PCDF are limited by legal regulations, it is necessary to check the emissions of polychlorinated dioxins and furans periodically. Due to the changes of the incinerated material, the dioxin emissions undergo a great variation in composition and intensity. For that reason, P. Ruggenthaler demanded a permanent surveillance of PCDD/PCDF emissions.
A system for permanent monitoring of polychlorinated dioxins and furans was briefly introduced by P. Ruggenthaler in 1992. Thereafter, the system was developed by Austrian E&E to an automatic sampling system with periodic off-line analytical measurements and installed at the Hazardous Waste Incinerator of the Municipal Waste Disposal Unit Simmering (EBS) in Vienna May 1993.
Based on the dilution method of dioxin measurement, the system isokinetically sucks a continuous flow of flue gas and accumulates PCDD's and PCDF's at a limited temperature. The sampling period was extended to 14 days. Any shut-down of the incinerator is immediately recognized, which enables the device to stop and start automatically.
The measurement cycle was repeated every two weeks, 26 times a year, and therefore, a continuous observation and documentation of the dioxin emissions from the hazardous waste incinerator was possible. The data and figures of the surveillance have been published periodically.
Based on the experiences of one year, we now present and discuss the observed recovery rate of the internal standard as well as changes in concept and design, and the reliability of this system.
In this paper the confidence limits of O_8CDD are presented and discussed as an example.

2. Reliability of the system

The system described at the "dioxin '93" was installed in May 1993 in the Waste Disposal Unit Simmering (EBS) in Vienna.
A final check of the reliability of the results was performed by comparing the measurement value determined by the system with eight (8) single emission rate measurements according to VDI 3499. The following table shows the dixon toxicity equivalents (TEQ) of the single measurement and that of the permanent dioxin monitoring system.
Table:
Results of single measurements and of permanent dioxin monitoring system (DMS), September 1993:

	Date	No.	TEQ [ng/m³]
single measurement	20.9.93	1	0.00074
	21.9.93	2	0.00053
	22.9.93	3	0.00068
	23.9.93	4	0.0006
	27.9.93	5	0.00362
	28.9.93	6	0.00069
	29.9.93	7	0.0008
	30.9.93	8	0.00024
DMS measurement	16.9. till 30.9.93		0.00047

The extremely low emission rate of dioxins is a result of the excellent performance of the flue gas cleaning system and has to be considered as a reason for a higher difference between the measurement values.

The mean value of seven (7) measurements (the value from 27.9.1993 seems to be out of range) can be calculated as

0.00067 ± 0.00059 ng/m³ (confidence limit of 95 %)

while the monitoring system shows

0.00047 ng/m³

(based on flue gas under nominal condition with 11 % O_2).

3. Recovery rate of the sampling as observed in the 1st year

Before sampling the glass fibre filter is spiked with recovery standard (1,2,3,4 ^{13}C-T_4CDD). After two weeks of sampling, the filter unit (including the mixing chamber) is completely replaced. In the laboratory the loaded filter unit is spiked with a mixture of all ^{13}C-2,3,7,8-standards. The glass fibre filters and the PU-foams are analysed according to the VDI guideline 3499 and as described at the "dioxin 93". Identification and quantification is performed by a mass-selective detector (HP 5971). The recovery rate of the measurement was calculed every 2 weeks. The mean recovery rate during the first year was 92%.

4. Changes in design and concept due to experiences of the 1st year

According to figure 1, the permanent monitoring system now is divided into two (2) principal parts (sampling unit and control unit). To reduce costs we optimized number and function of the components. The control unit now is a modular system.

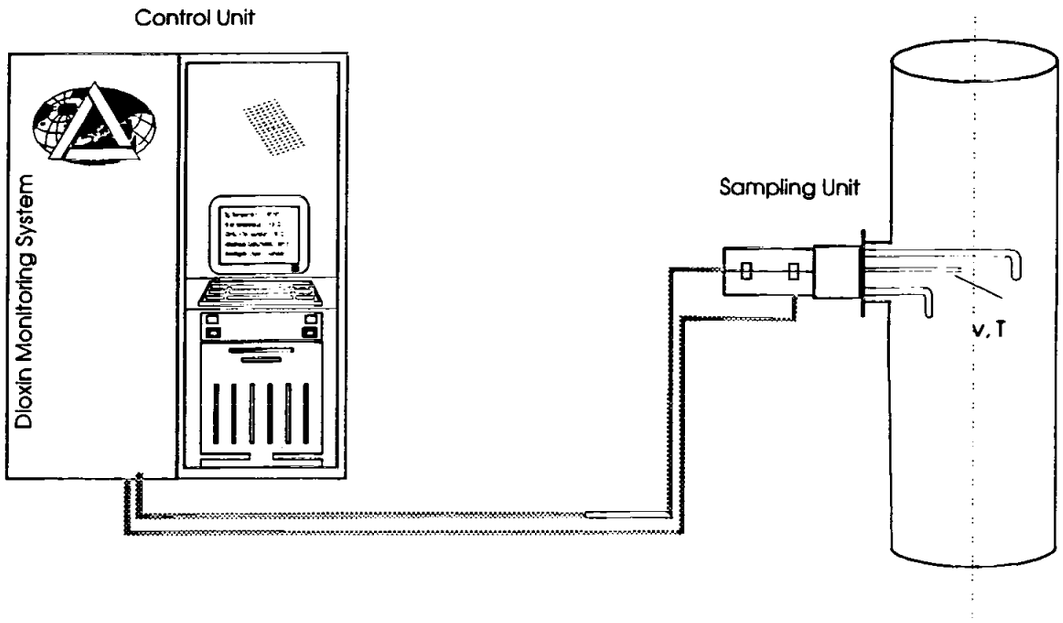


Figure 1: arrangement of the permanent monitoring system

The sampling filter now consists of two (2) independent tubes with nozzles to ensure permanent availability. Flue gas is sucked from two (2) different positions, which are switched by ball valves periodically. In the mixing chamber the flue gas is mixed with conditioned air and filtered afterwards. The filter consists of a glass fibre filter (0,1 m^2 area) and two (2) polyurethane foam mats (PUR) precleaned with toluene. An additional cleaning with acetone is not necessary. To avoid reactions inside the filter unit and for better handling only titanium is in contact to the flue gas.

The sampling and control unit have 5 main functions:

1) the flue gas is cooled to a temperature below 50° C without condensation (inhibitation of reactions between other flue gas compounds and PCDD/F)
2) quantitative accumulation of all PCDD/F by ad/absorption
3) ensure isokinetic sampling
4) stop of sampling in case of plant shut down (stand by mode)
5) restart sampling after plant restart

To evaluate the final concentration level, 3 measurement figures are necessary:

1) the absolute amount of PCDD's and PCDF's as determined in the laboratory
2) the total volume of flue gas sucked by the monitoring system
3) the oxygen content of the flue gas

To optimize the sampling conditions the following parameters are controlled:

1) temperature of dilution air, flue gas and mixed flue gas and air
2) ratio of dilution air/flue gas

The documentation of these parameters gives a sufficient evidence of proper function. After very good recovery rates we raised the amount of sucked flue gas to yield better confidence limits as discussed in chapter 5.

5. Confidence limits of the measured dioxin emissions

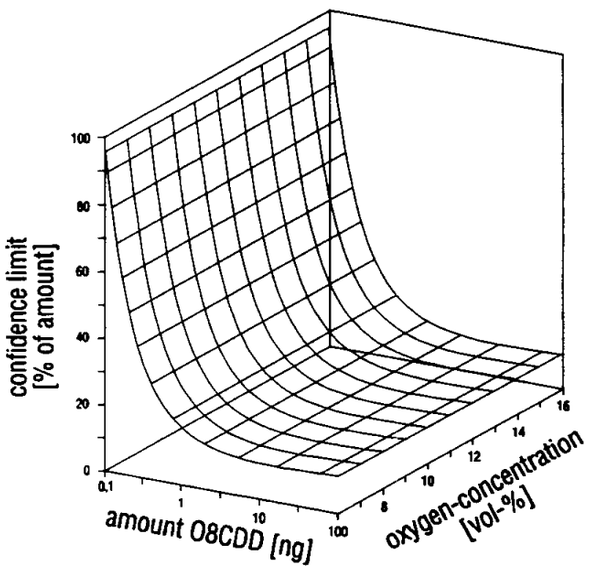
For interpretation of the results, the confidence limits are of interest. By keeping of all 5 main functions the confidence limit of the whole measurement mainly depends on:

1) volume errors of gasometers (dependent on the ratio of dilution air/flue gas)
2) errors of the oxygen measurement
3) validation data of the 17 toxic PCDD/F

As an example figure 2 shows the confidence limits of O8CDD in dependence of amount and oxygen contents. The graphic in figure is based on the following assumptions:

1) the error of both gasometers are 2 rel%
2) the error of oxygen measurement is 0,1 Vol%
3) use of weighted regression for the analytical calibration curve

Figure 2 shows the confidence limit decreases with increasing amount of O8CDD in the sample; especially with increasing amount of flue gas sampled.



6. Conclusions

Based on these results, the permanent monitoring system is suiteable and very reliable to observe the emissions of dioxins and furans during the entire on-stream operation.
The accumulation of PCDD/F reaches a high percental value due to high recovery rates of internal standard (92%) as described. Compared to manual measurements (VDI 3499) the mean recovery rate observed is very good.
Compared to a 6 hours measurement the confidence limits are much better, because of a greater amount of PCDD/F is enriched. Figure 2 shows, that confidence limits below 20 rel% at the actual legal limit of 0,1 ng TE/m³ are possible by using this permanent monitoring system.

7. References

1 VDI Guideline 3499, Düsseldorf/Germany, March 1990
2 Ruggenthaler P., Kahr G., Schmid E., poster at "dioxin 93"