Permanent Monitoring of PCDD/PCDF from a Hazardous Waste Incinerator

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1. Abstract

A permanent monitoring system to control polychlorinated dioxins and furans was briefly introduced by P. Ruggenthaler in 1992. The system was thereafter developed to an automatic sample-taking system with periodic off-time measurements.

Based on the dilution method of dioxin measurement, the system isokinectically sucks a continuous flow of flue gas and allows to extend the sampling period of 14 days. A shut-down of the incinerator is recognised by the increase of oxygen in the flue gas which enables the device to stop or start automatically.

By repeating the measurement cycle bi-weekly (26 times a year), a continuous observation and documentation of the dioxin emissions is possible by means of this device.

2. Introduction in Austria

Since the emission rates of PCDD/PCDF are limited by legal regulations, it is necessary to periodically check the emissions of polychlorinated dioxins and furans. Until now the emissions of municipal and/or hazardous waste incinerators were controlled by checking once a year. The emission rates obtained refer only to the plant operation during the time of measurement: six (6) hours a year.

Due to the changes in the composition 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 the PCDD/PCDF emissions instead of a one-week test only once a year. Afterwards, the data and figures of that surveillance have to be published for the public.

The surveillance of dioxins and furans is linked with certain problems:

It is not possible to control PCDD/PCDF directly like CO or SO_2 due
- to the low concentrations (pg/m^3) and
- to the portioning of PCDD/F between fly ash, gaseous phase and aerosols

Therefore, it is useful to separate sampling and analysis from each other for the permanent monitoring. The sampling device precipitates all of the particles to avoid aerosols and to adsorb the gaseous congeners. During off-stream operation the sampling has to be stopped until the unit starts up again. Long-term sampling during manual operation is not possible, therefore an automatic sampling device (permanent monitoring system) was developed to achieve these demands.

The first permanent monitoring system was installed in May 1993 at the Hazardous Waste Incinerator of the Municipal Waste Disposal Unit Simmering (EBS) in Vienna.

3. Structure of the Permanent Monitoring System

According to Figure 1, the permanent monitoring system is divided into three (3) principal parts (sample-taking filter unit, control unit and air-condition unit).

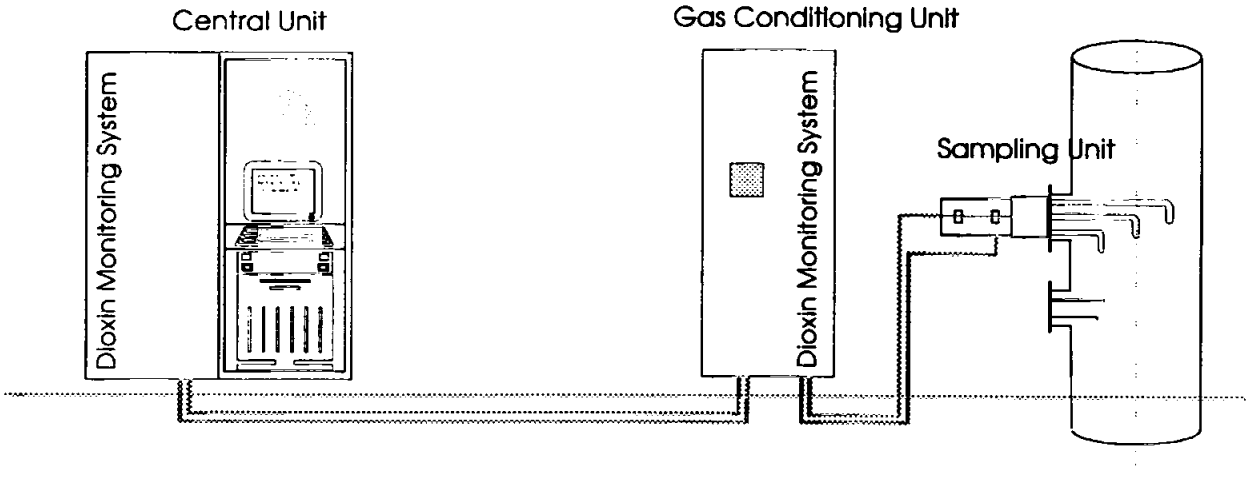

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Figure 1: arrangement of the permanent monitoring system

3.1 Sample Taking and Filter Unit

The sample consists of at least two (2) independent tubes with nozzles to ensure permanent availability. It is possible to suck flue gas from different positions over the complete length of the flue gas duct.

The filter unit has two (2) functions:

1. It acts as a mixing chamber, where the flue gas is mixed with clean, cooled and dried air.

2. It acts as a filter to accumulate the different dioxins and furans.

The sample-taking units are independently operated by ball valves. The filter unit is a combination of a mixing chamber, where the flue gas is mixed with conditioned air and filtered afterwards. The filter consists of a glass fibre filter (Schleicher & Schüll No. 9) and two (2) polyurethane foam mats (PUR) precleaned with acetone and toluene according to Guidline VDI 3498[2]. The filter unit is connected to the control unit and the air-conditioning unit. To avoid reactions inside the filter unit, only glass and titanium are used as element materials.

3.2 Control Unit

The control unit regulates the amount of sucked flue gas to ensure the isokinetic sampling and regulates the amount of sucked gas according to operating conditions to ensure the best possible efficiency. The control unit consists of following parts:

1. calibration instrument
2. output for maintenance
3. control system, Siemens Teleperm M
4. signal transformation (A/D)
5. recording instrument for permanent documentation

In the case of plant shut down the control system recognizes the rising oxygen content in the flue gas and stops the measurement operation automatically. The moment the plant starts up again, the oxygen content decreases and the control unit starts measuring again.

To evaluate the final concentration level, two measurement figures are needed:

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.

The operation parameters of the system must be checked permanently: these are the temperature in the mixing chamber, the condition of diluted air, the operation time and automatic starts/stops.The calibration of the system is made once a month by the maintenance engineer.

3.3 Air Condition Unit

This unit conditions the air (drying, cooling and filtering) and is located as near as possible to the filter unit.

4. Documentation

Documentation of the measurement is done by recording the following data:

1. oxygen content in the flue gas (checks the operation time of the incinerator)
2. temperature of the flue gas
3. total amount of sucked flue gas
4. sucked amount of flue gas per hour (actual value of sampling)
5. amount of flue gas per hour (actual value of the plant)
6. temperature in the mixing chamber

The documentation of these five (5) parameters gives a sufficient evidence of proper function.

5. Analysis

Before sampling, the glass fibre filter is spiked with recovery Standard (1,2,3,4, 13C-T4CDD). 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 13C-2,3,7,8 -Standards. The glass fibre filters and the PUR-foam mats are extracted with toluene and are cleaned according to the VDI Guidline 3499. The cleaned extract is evaporated to 100 µl and is injected into GC-MS.

The PCDD's and PCDF's are separated in the SP 2331 column. Identification and quantification is made by a mass-selective detector (HP 5971). By repeating the measurement period bi-weekly (26 times a year), a complete and continuous observation of the dioxin emissions is achieved.

6. Long-term Precipitation of PCDD/F on the Filter Unit

From the VDI 3498[2,3] it is known that PUR-foams are useful to precipitate PCDD's and PCDF's in ambient air with high recovery rate. To investigate the desorption behaviour of precipitated PCDD's and PCDF's on the filter unit (glass fibre filter, two (2) PUR-foams mats), a dissertation (4) was made. In this paper the temperature, flux per hour and total flux were varied to observe their influence. Based on the results of the mentioned thesis, the following parameters for operation of the permanent monitoring system are required:

1. temperature in the filter unit	< 50 °C
2. flux through the filter unit	< 6 m³/h flue gas + conditioned air
3. total flux	< 200 m³ flue gas

7. Operation

The system described above was installed in May 1993 in the Waste Disposal Unit Simmering (EBS) in Vienna. The engineering design of the system is based upon the following flue gas conditions:

flue gas velocity	5 - 15 m/s
flue gas temperature	90 - 130°C
max. dust content	20 mg/m³

8. Reliability of the System

A final check of the reliability of the results was made 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 dioxin toxicity equivalents (TEQ) of the single measurement and that of the permanent dioxin monitoring system.

Table:

Results of Single Measurements and of the 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.		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 discrepancy of 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

$$0.00067 \pm 0.00059 \text{ ng/m}^3$$

while the monitoring system shows

$$0.00047 \text{ ng/m}^3$$

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

9. Conclusions

Based on these results, the permanent monitoring system is suitable and very reliable to observe the emissions of dioxins and furans during the entire on-stream operation. Operation data of the permanent monitoring system are available since September 1993.

10. References

1 VDI Guidline 3499, Düsseldorf/Germany, March 1990
2 VDI Guidline 3498, Düsseldorf, Germany, January 1993
3 Tashiro Cetal, Comparison of High Volume Sampling Techniques for Dioxins and Furans in Ambient Air, Chemosphere, Vol. 19, Nos. 1-6, pp 1-6, 1989
4 Amini P., Dissertation at the Technical University of Vienna, 1993