# PERMANENT MONITORING OF POLYCHLORINATED DIOXINS AND FURANS IN FLUE GAS

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## 1. Abstract
A permanent monitoring system to control polychlorinated dioxins and furans was briefly described by Ruggenthaler in 1992 as a system for sample taking and off time measuring and was afterwards developed. Based on the dilution method[1] of Lützke the presented device allows, to extend the sampling period to 14 days. By repeating the measurement period 26 times a year, a continuing observation and documentation of the dioxin emissions is now possible.

## 2. Introduction
Since regulations limiti the emissions of PCDD/PCDF it is necessary to check periodically the emissions of polychlorinated dioxins and furans. Until now the emissions of municipal or hazardous waste incinerators are controlled by sampling flue gas for 3 to 10 hours once a year. The obtained emission values refer only to the plant operation during measurement time. Due to the complex nature of dioxin formation and precipitation changes of the dioxin emissions it can happen during plant operation and therefore Ruggenthaler demanded a permanent control to make the results accessible to 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 small concentrations ($pg/Nm^3$)
to the partioning of PCDD/F between fly ash , aerosols and gasphase.

Therefore it is usefull to seperate sampling and analysis for permanent monitoring. The sampling device has the job to precipitate all of the particles, to avoid aerosols and to adsorb the gaseous congeners. During operation breaks the sampling has to stop until the operation starts again. For long

time sampling manual operation is not possible, therefore an automatic sampling device (permanent monitoring system) which matches the demands was developed.

The first permanent monitoring system was installed in May 1993 at the municipal waste incinerator in the Entsorgungsbetriebe Simmering.

### 3. Structure of the permanent monitoring system

According to figure 1, the permanent monitoring system is structured into 3 principal parts (sample probes and filter unit, control unit and air condition unit).

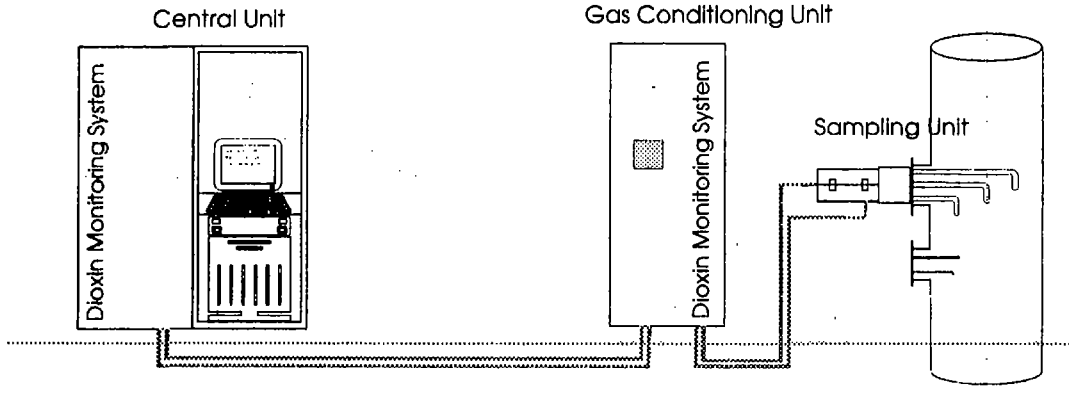


Figure 1: arrangement of the permanent monitoring system

### 3.1. Sample probes and filter unit

The sample probe consists of at least 2 independent probes, to ensure permanent availability. The probes are switched by ball valves. The filter unit is a combination of a mixingchamber ,where the flue gas was mixed with conditioned air and the filter. The filter consists of a glass fibre filter (Schleicher & Schüll No. 9) and two polyurethane foams (PU) precleaned with acetone and toluene according to Guideline VDI 3498[2]. The filter unit is connected to the control unit and the air condition unit. To avoid reactions inside the filterunit, the materials glass and titan are only used.

### 3.2. Control unit

The control unit regulates the amount of sucked flue gas according to isokinetic sampling and regulates the amount of sucked air according to operation conditions with the best possible recovery. The control unit consists of following parts:

1.) calibration instrument
2.) output for maintenance man (engineer)
3.) control system Siemens Teleperm M

4.) signal transformation (A/D)
5.) recording instrument for permanent documentation

In the case of a plant stop, the control system recognizes this because of the raisening oxygen content in the flue gas and stops the measurement automatically. The moment the plant starts working again, the oxygen content sinks and the control unit starts the measurement again.

Calibration of the system is performed once a month by the maintenance engineer.

### 3.3. Air condition unit

This unit has to job to condition the air (drying, cooling and filtering) and is situated as nearest as possible to the filter unit.

### 4. Documentation

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

1.) oxygen in the flue gas
2.) temperature of the flue gas
3.) amount of flue gas/hour (set point) due to isokinetic sampling
4.) sucked amount of flue gas/hour (actual value)
5.) total amount of sucked flue gas
6.) temperature in the mixing chamber

### 5. Analysis

Before sampling the glass fibre filter is spiked with recovery standard (1,2,3,4 13C-T4CDD). After 14 day sampling the filter unit (including the mixing chamber) is exchanged completely. In the laboratory the loaded filterunit is spiked with a mixture of all 13C-2,3,7,8 -standards. The glass fibre filters and the PU-foams are extracted with toluene and are cleaned up analogous to VDI guideline 3499. The cleaned extract is evaporated to 100 µl, 5 µl are injected into GC-MS. Separation of the PCDDs and PCDFs is done on SP 2331 column, identification and quantification is done with a mass-selective detector (HP 5971). By repeating the measurement period 26 times a year, a complete and unbroken observation of the dioxin emissions is obtained.

### 6. Longtime precipitation of PCDD/F on the filter unit

From the VDI 3498[2,3] it is known that PU-foams are usefull to precipitate PCDD's and PCDF's in ambient air with high recovery. To investigate the desorption behaviour of precipitated PCDD's and PCDF's on the filter unit (glass fibre filter, 2 PU-foams) a diplom work (4) was started. Temperature, flux/hour and total flux were varied to see their influence. Based on the

results following conditions are limited for operation of the permanent monitoring system:

1) temperature in the filter unit < 40°C
2) flux through the filter unit < 6 Nm³/h flue gas + conditioned air
3) total flux < 200 Nm³ flue gas

## 7. Operation

The described system was installed in May 1993 in the Entsorgungsbetriebe Simmering. The installed system is concepted for the following flue gas conditions:

| | |
|---|---|
| flue gas velocity | 5 - 15 m/sec |
| flue gas temperature | 90 - 130°C |
| max. dust content | 20 mg/Nm³ |

Figure 2: installed system in the Entsorgungsbetriebe Simmering

## 8. Conclusions

Based on the first results, the permanent monitoring system is suitable to observe the emissions of polychlorinated dioxins and furans during the whole operation time. In September 1993 operation data of the permanent monitoring system will be available.

## 9. References

1 VDI Richtlinie 3499, Düsseldorf/Germany, March 1990
2 VDI Richtlinie 3498, Düsseldorf/Germany, January 1993
3 Tashiro C et al, 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., diplom work at the Technical University of Vienna, 1993